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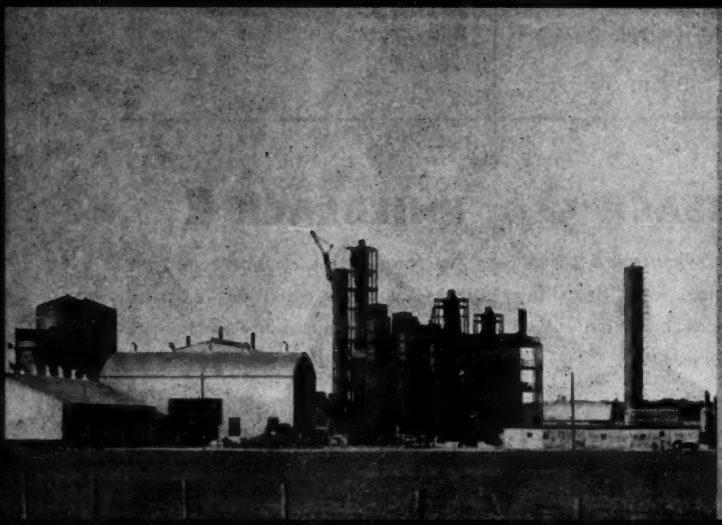

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Tensile, p. s. i.	2200	2600	2380	2250	1500
Elongation, %	530	410	300	350	380
Shore Durometer	42	68	70	61	45
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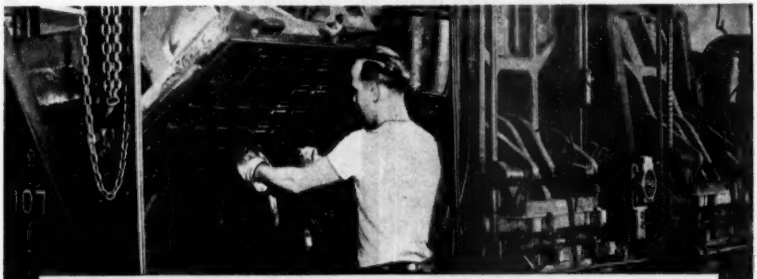

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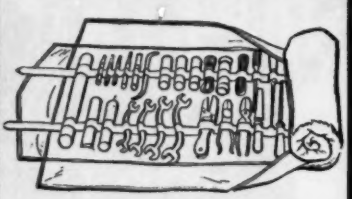

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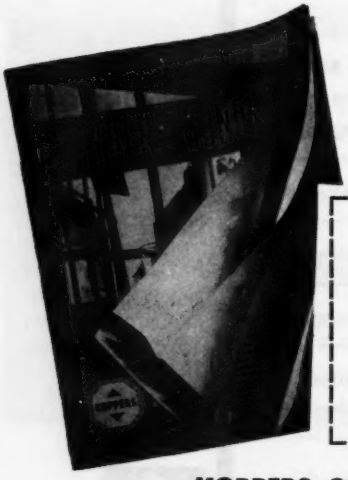

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NEW BOOKS AND OTHER PUBLICATIONS

RUBBER RED BOOK. 1953–54 Edition, Ninth Issue. Published by *Rubber Age*, 250 W. 57th St., New York 19. Cloth, 6 by 9 inches, 1,198 pages. Price, $10.—This series continues to grow in size; the new edition shows an increase in total number of pages, including advertisements, of 84. The general format and appearance are unchanged, although each section has been revised and brought up to date. Innovations in this edition include a special section devoted to export agents and the inclusion of the full names of company officers and executives in the alphabetic listing of rubber manufacturers.

The directory is divided into sections covering rubber manufacturers in the United States and Canada; rubber machinery and equipment; laboratory and testing equipment; accessories and fittings; rubber chemicals and compounding materials; fabrics and textiles; natural rubber and related materials; synthetic rubbers and other rubberlike materials; reclaimed rubber; scrap rubber and plastics; latex and related materials; miscellaneous products and services; consulting technologists; sales agents and branch offices; export agents; educational courses in rubber chemistry and technology; trade and technical organizations; technical journals; who's who in the rubber industry; and both subject and advertiser indexes. [From the *India Rubber World.*]

LATEX IN INDUSTRY. Second Edition, 1953. By Royce J. Noble. Published by *The Rubber Age*, 250 West 57th St., New York 19, N. Y. Cloth, 6 × 9 inches, 912 pages. Price, $15.00.—A comparison of this new edition with the first edition, published in 1936, provides one with a good measure of the rapid growth of the latex industry during the intervening period. Whereas the first edition contained 384 pages, this new edition is a weighty tome of 912 pages, including 400 pages of bibliography. It covers the practical aspects of both natural and synthetic rubber preparation, testing, and application.

The material is divided into three main divisions. Part I is made up of ten chapters, and deals with the preparation, compounding, and properties of latex. Natural latex, its preservation, concentration, and shipment are covered in detail. Synthetic latexes, rubber dispersions, vulcanized latex, general compounding materials and practices, coagulation, and vulcanization of latex rubber deposits are also treated in this section. Part II, fourteen chapters, covers the industrial applications of latex. Detailed information is given on all the important processes, such as impregnation, spreading, dipping, casting, electrodeposition, foamed latex, thread, and adhesives. Part III, one 102-page chapter, deals with the testing of latex and latex compounds, and includes methods for sampling, determination of total solids, dry-rubber content, rubber hydrocarbon, coagulum, strainability, sludge, alkalinity, KOH number, mechanical and chemical stability, surface tension, viscosity, etc.

Procedures for preparing and testing latex films are included. Stress-strain properties, aging, density, water absorption, Mooney viscosity, ash, extractables, sulfur, copper, and manganese are described. In addition, procedures for identifying natural and synthetic rubbers and for the control testing of common compounding ingredients are given.

The chapters on compounding and dipping give the impression of being especially authoritative. However, the chapter on "Porous Rubber", which

includes foamed latex, seems to have been given too light treatment, particularly since foamed latex is now such an important material and accounts for the greater part of the latex used. The text on rubber thread seems a bit generalized.

This new edition of Noble's earlier work is directed toward the practical man and contains little for the theorist. It is a valuable addition to the technical literature of rubber, and should be readily accessible to everyone concerned with the technological aspects of the production and use of latex. In addition to practical workers in the field, it is recommended also as a handy reference volume for technical sales, and for legal and management personnel. [Leonard A. Wohler.]

RUBBER—A STORY OF ROMANCE AND SCIENCE. United States Rubber Co., Rockefeller Center, New York 20, N. Y. 34 pages.—This brochure, a resived edition of a similar U. S. Rubber publication entitled, "Romance of Rubber", describes the collection and preparation of natural rubber, the manufacture of synthetic rubber, and the applications to which these materials are put. Profusely illustrated, the booklet is intended to acquaint school children with the rubber products they use. [From the *India Rubber World.*]

RUBBER AND PLASTICS USED IN THE PRINTING INDUSTRY. PL-3. Research & Engineering Council of the Graphic Arts Industry, Inc., Washington, D. C. Paper, 8½ by 11 inches, 24 pages. Price, $3.—Intended as a broad guide both to the industry and to manufacturers and suppliers of rubber and plastic materials, this brochure outlines the use of these materials in printing applications. The preparation and use of rubber printing plates, including types, molds, handling, and limitations, and of plastic plates (thermosetting and thermoplastic), including inks, adhesives, molds, etc., are described in detail. [From the *India Rubber World.*]

ORGANIC COATING TECHNOLOGY. VOLUME I. OILS, RESINS, VARNISHES, AND POLYMERS. By Henry Fleming Payne. John Wiley & Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 6×9 inches, 674 pages. Price $10.00. This volume, the first of a series of two, covers the manufacture, chemistry, and use of the principal materials employed in the coating industry. The fundamental chemistry of the base materials, solvents, driers, plasticizers, and other ingredients is presented. The several types of each group of film-forming substances are listed, with a comprehensive description of their usage and properties, both in the processing and in the finished states. Probably of greater interest to the plant chemist is the large number of practical formulations, with tables and discussions pertaining to the applications, processing conditions, and properties of these formulations.

Fifteen chapters treat of the fundamentals of film formation, vegetable and marine oils, varnish resins, driers, solvents, resins of the alkyd, urea-formaldehyde, and melamine-formaldehyde types, rubber resins, plasticizers, cellulose polymers, resins of the vinyl, acrylic ester, and silicone types, and an excellent chapter on test methods. The chapter on rubber resins treats briefly of the chemical compositions and properties of natural and synthetic rubbers, and more extensively of chlorinated rubber (Parlon), cyclized rubber (Pliolite), chlorinated biphenyls (Arochlor), chlorinated paraffins (Chlorafin and Chlorowax), and synthetic-rubber latexes.

The author's inclusion of a few philosophical reflections gives this volume a friendly atmosphere not usually encountered in technical literature. [H. S. Anthony, Jr.]

ASTM Standards on Textile Materials (with Related Information). Published by American Society for Testing Materials, 1916 Race St., Philadelphia 3, Penna. 6×9 in. 696 pp. $5.25.—This 1953 compilation of ASTM Standards on Textile Materials brings together in compact readily usable form the ASTM specifications, test methods, and tolerances widely used in this field. Prepared by ASTM Committee D-13 on Textile Materials, this edition gives in their latest form 105 ASTM standards, including 80 test methods; 17 specifications; 2 definitions of terms relating to textile materials; 3 tolerances for filament yarns (acetate-nylon-rayon); 3 recommended practices: one for interlaboratory testing of textile materials—another for designation of linear density of fibers, yarns, and other textile materials in universal units—and one for designation of yarn construction; and other material. Groups of standards in this compilation cover: asbestos, bast and leaf fibers, cotton, glass textiles, rayon, acetate and silk, wool, pile fabrics (carpets), felt; and general fibers, fabrics, yarns, threads, and cordage. Also, identification, qualitative, and quantitative analysis; and resistance to insect pests and microorganisms. General test methods cover testing machines, humidity, and interlaboratory testing. A convenient table of contents is included (by subject and ASTM serial designation) as well as an extensive index. [From *The Rubber Age.*]

The Van Nostrand Chemist Dictionary. Published by the D. Van Nostrand Co., Inc., 250 Fourth Ave., New York 3, N. Y. 6×9 in. 762 pp. $10.00.—This is a new type of chemical dictionary which has been designed to meet the needs of the present-day chemist and chemical engineer. It contains over 11,000 definitions of laws, equations, reactions, tests, solutions, laboratory apparatus, and industrial processes and equipment. Both proper-name terms and common names are included so that, for example, the user can locate the law of the rectilinear diameter as well as the law of Gay-Lussac or the Langmuir adsorption isotherm as well as the equation of continuity. The definitions in the book, prepared by a special board of editors, are specifically shaped for the use of the chemist. The equations and laws are clearly explained, and their range of application is indicated. The solutions and tests are outlined in detail, including the quantities of reagents and the steps in the preparation or analysis. The type compounds, radicals and reactions are given with structural formulas and equations. These definitions range in size from a few words to comprehensive articles, several pages long. This new dictionary is a valuable work tool for the chemist and engineer and a welcome addition to the technical bookshelf. [From *The Rubber Age.*]

The Firestone Story. By Alfred Lief. Published by the McGraw-Hill Book Co., 330 West 42nd St., New York 36, N. Y. 6×9 in. 438 pp. $4.50.—Covering the first 50 years of the Firestone Tire & Rubber Co., this book gives not only a close-up of Harvey Firestone, Sr., but a glimpse into American history. It is a book about American inventiveness, industry, and character; a story of the growth of a free competitive economy from its inception through 1950. Mr. Lief spent more than three years doing the research for the book, and during this time the archives of the Firestone organization were completely

at his disposal. He also gathered much of his information from friends and employees of Mr. Firestone. Since the story of the Firestone organization lies in the reflected shadow of its founder, the book is biographical to a large extent. This book takes its place along with the "House of Goodyear" as a factual report of the growth of one of America's formost rubber manufacturing concerns. [From *The Rubber Age.*]

SILICONES AND THEIR USES. By Rob Roy McGregor. Published by McGraw-Hill Book Co., Inc., 330 West 42nd St., New York 36, N. Y. 5½×8 in. 302 pp. $6.00.—The available information on the numerous types of silicone products is ably correlated in this work. The properties, preparation and applications of these fascinating materials are described in nontechnical language to give the reader an overall picture of what silicones are and what they can be used for. Types of commercial products covered include silicone rubber, silicone fluids, silicone compounds, silicone lubricants, silicone resins, and "bouncing putty". Representative industries and the uses they are making of silicones are tabulated and techniques of application shown. Preparation of silicones from raw material to the finished product is explained in an elementary manner to make this information equally helpful to both chemists and non-chemists. The section on silicone rubber covers 36 pages and treats of chemical and physical properties, preparation of the rubber, types available, and numerous commercial applications in the form of dispersions, pastes, and stocks. The book has 5 chapters and a subject index. A list of 152 literature references is also included. [From *The Rubber Age.*]

WINNING THE BATTLE FOR MORE TIRE MILAGE ON PASSENGER CARS. Rubber Manufacturers Association, Inc., 444 Madison Avenue, New York 22, N. Y. 8½×11 in. 24 pp.—This publication describes and illustrates common abuses and misuses to which automobile tires and tubes are subjected. It contains many helpful hints for obtaining maximum service from automobile tire equipment. These are detailed in five sections relating to fabric injuries, tread wear, inflation, wheel balance, and inner tube troubles. Proper care of tires, the publication states, can make driving safer, assist in the efficient operation of the car, and save money.[From *The Rubber Age.*]

THE POLYMERIC STRUCTURE OF NATURAL RUBBER *

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British Rubber Producers' Research Association, Tewin Road, Welwyn Garden City, Hertfordshire, England

From the tree to the vulcanized article, the changes in the elastic properties of natural rubber are dependent on essentially second-order modifications of the parent polymer. Successfully in some ways, less so in others, rubber technologists have learned empirically how to develop advantageous qualities and to prevent or minimize the undesirable ones. This empiricism is inevitable because the chemical reactions which produce the physical changes are so little understood. For example, vulcanization represents the conversion of the chainlike polymer into a cross-linked network, but the nature, number, and distribution along the chain of the cross-links, and their variation with curing conditions and on subsequent aging are largely matters of speculation. In fact, one of the major impediments to scientific rationalization of rubber technology is the inability to interpret common physical observations, *e.g.*, on plasticity, state of cure, deterioration on aging, cracking, in terms of molecular structure.

The main chemical attack on the problem in these laboratories has been based on the rigorous, but necessarily long-term, course of first resolving the chemistry of a particular process with the aid of model systems, whereby product analysis and identification can be firmly established, and then determining how rubber behaves when caused to undergo similar reactions in a controlled manner. In other words, attention has been directed to the *atomic* details of aging, vulcanization, etc., rather than to their significance in modifying *polymer* structure. Our purpose here is to lay emphasis on the latter approach, first by surveying briefly the main physical changes encountered in rubber technology, and then, stimulated by some very recent work on the nature and degradation of raw rubber, by tracing certain fundamental factors underlying these phenomena.

THE POLYMERIC NATURE OF RAW RUBBER

In contrast with the long-standing recognition that the basic rubber substrate is comprised of isoprene units, its very high molecular weight has only recently been fully accepted. Critical studies by Gee[1] nearly fifteen years ago finally established that raw rubber, as known in Europe, has a mean molecular weight of the order of 350,000. He also showed that the so-called sol fraction approximates more closely to a linear long-chain polymer than does the "gel", the insolubility of the latter reflecting a cross-linked structure rather than a greater degree of polymerization. The relevance of these molecular-weight studies to the rubber produced by the tree is obscured by the obvious changes

* An original contribution to Rubber Chemistry and Technology from the British Rubber Producers' Research Association. The paper was presented at Les Journées du Caoutchouc, organized by l'Association Française des Ingenieurs du Caoutchouc and la Société de Chimie Industrielle, at the French Rubber Institute, Paris, June 24–29, 1953.

which occur on storage, and a prerequisite to assessing their overall significance was the extension of this work to fresh rubber.

Notable work by Bloomfield[2] in Malaya has now done much to effect this extension and has produced some unexpected findings. First, the essentially hydrocarbon fraction isolated from freshly tapped latex (collected under conditions minimizing contact with oxygen and extraneous bacteria) has a mean molecular weight very much higher (by a factor approaching 10) than Gee's value. Important changes evidently occur during the conventional coagulation and kindred processes and (or) storage. Some factors believed to contribute to these are considered in the next two sections. Second, the fresh hydrocarbon fraction is not homogeneous in physical form, but contains a substantial proportion (20–70 per cent, depending on clone and tapping conditions) of material not immediately soluble in benzene. This has been termed microgel, both to denote its difference from the ordinary gel fraction in readily giving a colloidal-like dispersion on shaking, and to express the similarity with a component of synthetic latexes in which cross-linking within the individual micelles is envisaged[3]. The fundamental significance of this observation is that rubber in its original form can no longer be assumed to be a linear polyisoprene, reactions having occurred during its biosynthesis or storage in the tree to produce cross-linking. An important practical consequence is that this basic and variable heterogeneity prevents any direct correlation being established between the different physical properties of rubber which are usually taken as dependent on molecular size. Thus, the microgel content has little influence on the solution viscosity, but contributes to the hardness of the coagulated rubber.

In summary, the so-called hydrocarbon component of natural rubber is a highly complex substance when it issues from the tree, both with respect to polymer type and size and, almost certainly, to chemical inhomogeneity.

DEGRADATION OF RUBBER IN SOLUTION

It is well known that solutions of rubber decrease in viscosity on standing at ordinary temperatures in the dark. This has commonly been associated with atmospheric oxidation. This view appears to be supported by the behavior of highly purified rubber and gutta-percha, where a parallelism can be traced between the rates and extents of oxygen absorption and decrease of viscosity[4]. Consistently, the addition of an oxidation inhibitor or catalyst retards or accelerates both these changes to a comparable degree.

With raw rubber, however, the situation is very different, and analogy with the oxidative scission of purified rubber is misleading[5]. Solutions of unpurified rubber degrade at almost the same rate in oxygen as in stringently evacuated systems, and oxidation inhibitors exert practically no stabilizing action (Figure 1). Further, under certain conditions where degradation proceeds readily, no absorption of oxygen can be detected.

The only acceptable conclusion consistent with all the experimental facts[5] is that some inherent feature of the rubber chain is responsible for an essentially spontaneous breakdown, which is largely immune from external environmental influences. This suggests that the basic rubber molecule, instead of being a uniform polyisoprene hydrocarbon, possesses a certain small proportion of "anomalous" bonds. Molecular weight measurements indicate that one such bond is, on the average, associated with about 10,000 isoprene units—further emphasizing that second-order structural features may be predominant in producing macroscopic physical changes. The identity of the odd bonds is very

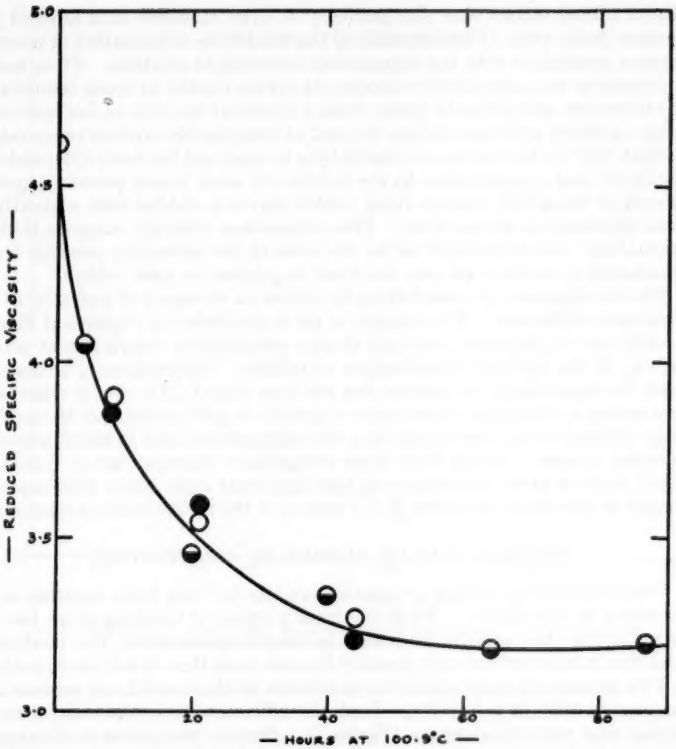

Fig. 1.—Decrease of viscosity of 0.25 gram smoked sheet in 100 cc. chlorobenzene at 100.9° C in vacuo with pyrogallol, and with measured amounts of residual air present.

◒— $<10^{-4}$ mm. O_2 + 0.1% Pyrogallol
○—1.31×10^{-3} mm. O_2 present
●—8.54×10^{-3} mm. O_2 present

difficult to specify, especially in view of their low energy content, but it is tempting to imagine that they represent fragments of functional groups or catalytic molecules concerned in the *in vivo* synthesis.

These findings are not only of potential biochemical interest, but have immediate practical consequences as regards the control of degradation in solutions kept in the dark (to eliminate the other important factor, photochemical degradation). It is of secondary importance to take elaborate precautions to exclude oxygen and to add oxidation inhibitors. In fact, the only practical factor or control is temperature, which should be kept as low as possible to minimize the spontaneous changes.

GELATION

Rubber has a pronounced tendency to convert itself in part into an insoluble and not readily dispersible macrogel. The presence of microgel in freshly

isolated rubber shows that this tendency is even manifest as a natural phenomenon in the tree. Consideration of the conditions of formation of macrogel reveals a parallelism with the degradation occurring in solution. Thus, macrogel formation is a nonoxidative process; it occurs readily at room temperature and, therefore, undoubtedly stems from a chemical reaction of low activation energy; gelation and degradation proceed at comparable rates at temperatures of about 100° C; the degree of cross-linking in macrogel has been independently calculated[6] and approximates to the number of weak bonds present[2]; and the removal of the gelled fraction from rubber leaves a residue with a greatly reduced spontaneous degradation. This comparison strongly suggests that the "anomalous" bonds thought to be the sites of the molecular scission during degradation in solution are also involved in gelation in solid rubber.

The development of cross-linking in rubber on storage is of practical as well as theoretical interest. The increase of gel is paralleled by changes of Mooney viscosity and is, therefore, relevant to any quantitative description of properties, *e.g.*, in the technical classification of rubber. Unfortunately, no practical means for suppressing the process has yet been found. Its rate is retarded to some extent by absorbed water vapor (increase in gel content and Mooney viscosity increase being accelerated in a dry atmosphere) and is uninfluenced by molecular oxygen. Apart from these preliminary observations of Wren[7] and Wood[8], there is little information on this important topic either with regard to changes in polymeric structure or the nature of the basic chemical reactions.

DEGRADATION OF RUBBER BY MASTICATION

Plasticization by milling or mastication has for long been essential in the processing of raw rubber. While the basic purpose of breaking down the rubber molecules into smaller fragments is readily appreciated, the method by which this is achieved has only recently become more than indefinite hypothesis.

Two apparently anomalous characteristics of the breakdown process have long proved difficult to explain. First, the efficiency of breakdown varies in a peculiar way with temperature (Figure 2). Second, the presence of oxygen is necessary for breakdown, but, at temperatures below 100° C, common oxidation inhibitors do not cause any appreciable retardation (Figure 3). A third feature more recently apparent is that, among synthetic polymers, there is no correlation between rate of breakdown on cold milling and susceptibility to oxidation.

Practically compelling evidence that the breakdown throughout the temperature range is not explicable by one type of degradation, but is a composite process represented by the curves (A) and (B) in Figure 2, has now been presented[9]. Curve (A) refers to degradation in which the primary step is a mechanical tearing apart of the molecules. As the temperature of mastication is increased and the rubber becomes softer, the shearing forces decrease, and the efficiency of breakdown steadily diminishes until it becomes negligible at temperatures above about 120° C. Curve (B), on the other hand, refers to degradation which is an accompaniment of direct oxidation of the rubber, and only becomes appreciable at temperatures above about 100° C. Oxygen is normally necessary for both processes, but for quite different reasons: in the higher temperature process it is a prime reactant; in the lower temperature process it acts merely in a secondary sense to prevent the recombination of the broken fragments. Accordingly, the two processes respond distinctively to the presence of other substances. Thus, while oxygen plays an essential role in hot

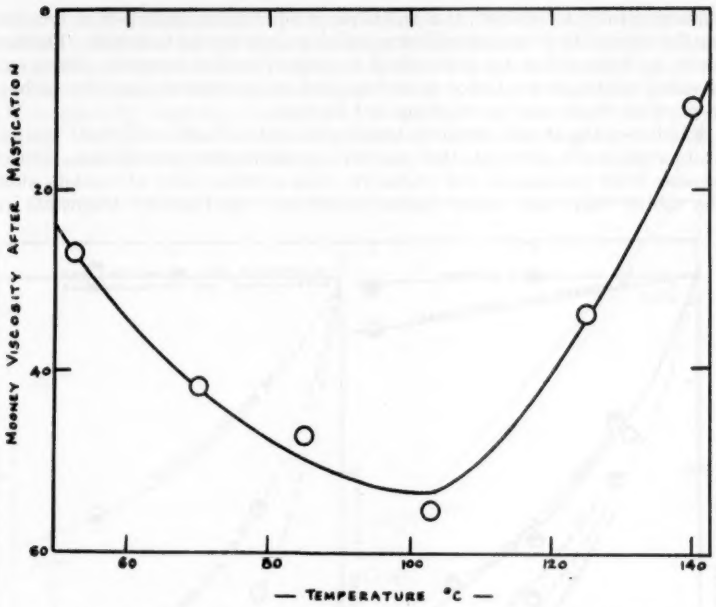

FIG. 2.—Efficiency of plasticisation *vs.* temperature of mastication. Mooney viscosities after 30 minutes' mastication in size-B Banbury.

mastication, in cold mastication the presence of other substances able to react with the primary fragments should result in rubber degradation. Numerous compounds have been found to do so, with efficiencies which vary in a parallel manner with their power of reacting with substituted allyl free radicals. Antioxidants, as such, are without effect. The reverse situation should be encountered in hot mastication, and this is strikingly illustrated for benzoquinone (a free-radical acceptor) and hydroquinone (an antioxidant) by the data presented in Figure 3.

The common function of free radical acceptors in interacting with the primary ruptured fragments does not necessarily result in the formation of masticated products of similar properties. For example, thiophenol and other hydrogen-transfer agents yield a soft soluble mass, while chloranil and maleic anhydride yield a dry, largely insoluble crumb. Such differences arise from the reactivity of the secondary product formed by reaction with the radical acceptor. With thiophenol, it is reasonable to assume that the primary hydrocarbon radicals merely abstract the mercapto-hydrogen atoms and thus produce a lower molecular-weight material, identical otherwise with the original rubber; with chloranil and maleic anhydride, secondary radicals are probably formed additively, and these have a great tendency to stabilize themselves by reacting with neighboring rubber chains to give cross-linked structures.

By the use of various additives, it is possible in this way to convert a linear polymer into a branched or cross-linked modification at will. Since the particular physical advantages of these different structures for certain purposes is

beginning to be recognized, this technique is potentially important in developing the versatility of natural rubber as a high polymeric raw material. Furthermore, we believe that the principle of fixation of radical acceptors during mechanical treatment is a factor in carbon black reinforcement, and also perhaps in physical effects such as cracking and tearing.

Although the atomic details of mastication in the "cold" and "hot" temperature regions are different, the polymeric consequences are similar. This is because both mechanical and oxidative chain scission occur at random along the rubber chain and, under normal conditions, the ruptured fragments are

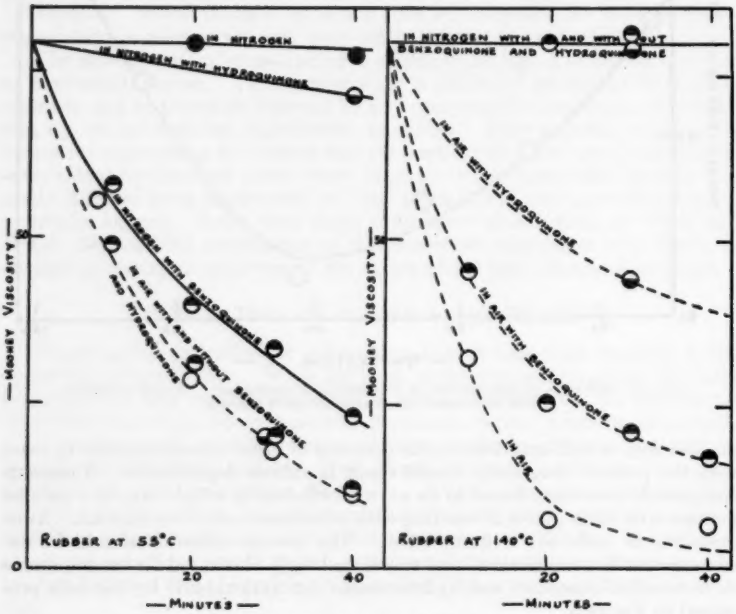
IN NITROGEN
IN NITROGEN WITH HYDROQUINONE
IN NITROGEN WITH BENZOQUINONE
IN AIR WITH AND WITHOUT BENZOQUINONE AND HYDROQUINONE
— MOONEY VISCOSITY —
RUBBER AT 55°C
— MINUTES —
IN NITROGEN WITH AND WITHOUT BENZOQUINONE AND HYDROQUINONE
IN AIR WITH HYDROQUINONE
IN AIR WITH BENZOQUINONE
IN AIR
RUBBER AT 140°C
— MINUTES —

FIG. 3.—Mastication of rubber in air and nitrogen, with and without added chemicals at 55° and 140° C.

Solid lines—mastication under nitrogen.
Dash lines—mastication in air.
—with benzoquinone added.
—with hydroquinone added.

stabilized without further reaction with other rubber chains. Hence, rubber degraded to the same extent by either process possesses the same distribution of chain lengths. This can be confirmed by making measurements depending differently on the distribution of chain lengths; for example (*cf.* final section), the relationship between Mooney and intrinsic viscosity of masticated rubbers is independent of the type of mastication (Figure 4).

VULCANIZATION

The profound changes in elastic and solubility properties shown by rubber on vulcanization denotes some characteristic alteration in polymer structure.

Although chemical details are only now beginning to be resolved, three distinct lines of evidence establish that the essential function of vulcanization is to convert the mixture of mainly linear molecules into a network-aggregate held together by primarily valency cross-links. First, a quantitative description of rubber elasticity, swelling, and related properties has been founded on this model[10]; second, conditions disrupting a rubber vulcanizate also degrade model substances containing sulfide linkages; third, the subjection of simple analogs

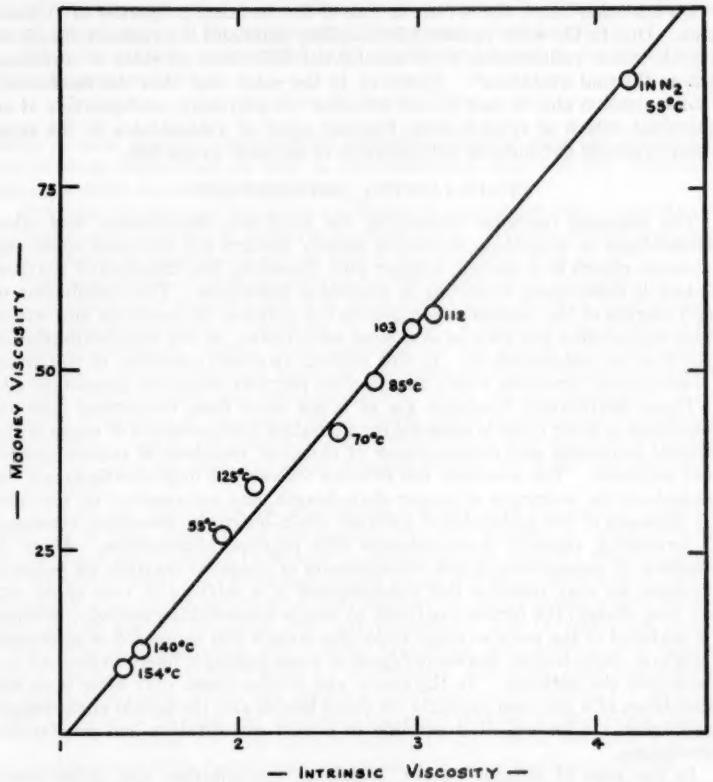

Fig. 4.—Uniform relationship between Mooney and intrinsic viscosity independent of the temperature or extent of mastication. Mastication for 30 minutes in air at the recorded temperatures.

of rubber to vulcanizing conditions produces molecular coupling. Particularly convincing evidence of the third type is the relatively simple coupling reactions of dialkyl peroxides and their derivatives with monomeric olefins and the production of good rubber vulcanizates under the same conditions[11]. Also, the ready noncoupling reactions of monothiols with olefins and the corresponding nonvulcanizing of rubber are to be compared with the coupling reactions of dithiols with olefins and corresponding production of rubber vulcanizates[12].

The physical properties developed depend primarily on the polymeric structure, *i.e.*, on the degree and distribution of cross-links rather than on their nature. All vulcanizing methods, independent of their chemical character, effect cross-linking at random along the polymer chains, and so the polymeric configuration of all vulcanizates at the same degree of cross-linking should be identical. For this reason, a wide range of vulcanizing procedures gives products with merely second-order differences of physical properties at equivalent extents of cross-linking.

On the other hand, the reverse is true of the chemical properties of vulcanizates. Due to the wide variation in coupling units and the residual chemicals present, sulfur vulcanizates show substantial differences of rates of reactions, such as thermal oxidation[13]. However, in the same way that the mechanism of vulcanization and its rate do not influence the polymeric configuration at an equivalent extent of cross-linking, thermal aging of vulcanizates to the same extent produces comparable deterioration in physical properties.

CHAIN-LENGTH DISTRIBUTIONS

The chemical reactions underlying the synthesis, degradation, and other modifications of long-chain molecules usually involve the monomer units and polymeric chains in a random manner and, therefore, the structure of the final product is determined according to statistical principles. The distribution of chain lengths of the molecules comprising the polymer on synthesis and subsequent degradation can then be evaluated statistically, as can the distribution of cross-links on vulcanization. In this section we direct attention to the forms of distribution functions which characterize polymer structure quantitatively.

These distribution functions are of much more than theoretical interest. Knowledge of their value is essential for a detailed interpretation of many of the physical properties and consequences of chemical reactions of rubber and related polymers. For example, the solution viscosity is disproportionately dependent on the molecules of longer chain-length, and information on the relative amounts of the molecules of different chain-length is, therefore, necessary for correlating viscosity measurements with polymer composition. As an illustration of dependence of the consequences of chemical reaction on polymer structure, we may consider the vulcanization of a mixture of very short and very long chains; the former are likely to escape cross-linking entirely, whereas in a material of the same average molecular weight but composed of molecules of uniform chain-length, the same degree of cross-linking is likely to bind all the chains into the network. In the above and similar cases, only after both the dependence of a physical property on chain length and the actual chain-length distribution are known, is it possible to obtain quantitative and predictable correlations.

In the case of natural rubber, fractional precipitation and other direct methods have shown that it is composed of molecules of a wide range of chain lengths. The data are too qualitative for deriving the chain-length distribution, and in view of the insolubility and colloidal nature of part of the rubber and the presence of different chemical species, it is unlikely that direct methods will yield exact information within the near future. Accordingly, it seems more advantageous at present to utilize the probable distribution functions discussed below in practical problems wherever the dependence of the relevant physical properties on chain-length is known. Correlation of predicted and experimental results then affords a test of the calculated distribution functions. For example, the distribution functions for masticated rubbers predict a linear rela-

tionship between the logarithms of the number-average and viscosity-average molecular weights, of slope a of the Houwink-Mark equation, $\eta = KM^a$.

Chain-length distribution on polymer formation.—Under a wide range of conditions, the chain-length distribution functions on formation of nonbranching polymer chains by polycondensation, ionic, and free-radical polymerizations are described by:

$$N_x/N = \beta e^{-\beta x} \tag{1}$$

where N_x is the number of chains of length x monomer units, N is the total number of chains, and β is the reciprocal of the average chain length[14].

When branching occurs during or after polymer formation, the distribution of chains is given by:

$$N_x/N = (\beta + \gamma)e^{-(\beta+\gamma)x} \tag{2}$$

where N_x now includes chain-lengths between molecular ends and cross-links, and between cross-links, as well as free molecules, and γ is the fraction of monomer units containing cross-links.

Function (1) thus appears to be applicable to elastomers where branching is negligible and function (2) where it is appreciable. Natural rubber may then be considered as represented by (2) with β and γ of the order of 10^{-4}.

Figure 5 gives a physical picture of rubber according to Equation (2). In relative number of chains, there is a preponderance of those of shorter chain length. In relative weight fractions, by contrast, a maximum is present at the average chain-length value. Even qualitatively the shapes of these number and weight fraction curves are useful in considering various polymer characterizations. For example, the large number of short chains necessitates in osmometry a membrane impermeable to chains much shorter than the average chain length. Again, the weight fraction curve indicates which middle fraction is likely to have the least variation of chain length, for direct application in fractionation.

Chain-length distribution on mastication.—Elastomers are readily classified according to their behavior on mastication into four classes: (1) initially linear chains which are degraded to shorter linear chains, *e.g.*, gel-free natural rubber and Neoprene WRT: (2) branched chains which are degraded without further branching, *e.g.*, most samples of natural rubber; (3) linear chains which become branched as well as degraded, *e.g.*, polybutadiene: and (4) branched chains which undergo degradation and further branching, *e.g.*, acrylonitrile copolymers. Statistical analysis[15] leads to distribution functions after mastication for these four cases, which are only modifications of Equations (1) and (2). (This result is to be expected as almost the same statistical conditions apply.)

Class (1) includes the cold and hot milling of elastomers, whereby the ruptured ends are stabilized without interaction with other rubber molecules. At an extent of degradation represented by α, defined as the fraction of monomer units at which rupture has occurred, the distribution after mastication is given by:

$$N_x/N = (\alpha + \beta)e^{-(\alpha+\beta)x} \tag{3}$$

$$= \alpha e^{-\alpha x} \quad \text{when} \quad \alpha \gg \beta \tag{4}$$

An interesting special case is for total recombination of ruptured ends, when an equilibrium distribution given by Equation (1) is obtained independent of the initial chain-length distribution, thereby providing a means of obtaining a material of known distribution from one of unknown initial distribution.

As stated above, natural rubber appears to exemplify a polymer conforming initially to Equation (2) and on ordinary mastication not becoming further branched (class 2). Its distribution function after mastication is:

$$N_x/N = (\alpha + \beta + \gamma)e^{-(\alpha+\beta+\gamma)x} \tag{5}$$

As degradation proceeds, the term β becomes progressively less important as α increases. The rapid dissolution of the gel fraction on light milling suggests that the branching links are preferentially ruptured with little overall break-

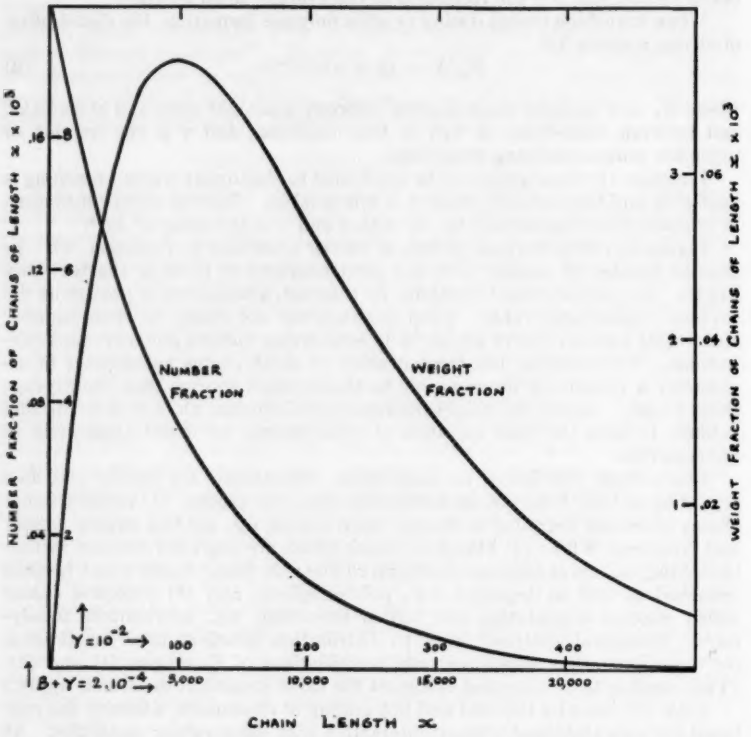

FIG. 5.—Distribution of chain lengths of raw and vulcanized rubber according to Equations (2) and (6). Scales outside ordinate and abscissa refer to raw rubber with β and γ both of value 10^{-4}. Scales inside ordinate and abscissa refer to a vulcanizate with γ of 10^{-2}.

down, *i.e.*, γ also decreases. On mastication, then, rubber rapidly passes from a distribution represented by the more general Equation (5) to forms (3) and (4), both of which are formally identical with Equation (1).

When a linear polymer undergoes both degradation and branching on mastication (class 3), the chain-length distribution changes from function (1) to function (5). In this case, α is the extent of degradation and γ the amount of accompanying cross-linking on mastication. The relative magnitudes of α

and γ determine the physical state of the masticated rubber. When α is large compared with γ, the elastomer is apparently degraded to the soluble product found for noncross-linking, and the influence of γ is only observed by more detailed measurement. For example, natural rubber with addition of aniline, *n*-butyramide, or benzoyl peroxide still remains soluble after milling, but these rubbers do not show the Mooney-intrinsic viscosity relationship of Figure 5 typical of linearly degraded rubber[9]. On the other hand, when γ increases more rapidly than α, cross-linking is favored, compared with degradation. It is characteristic of all cross-linking processes that the binding of molecules into network structures proceeds with almost discontinuous change in rate after a certain critical value[6] of γ. Hence, as expected, mastication frequently produces a high proportion of the rubber as a cross-linked network and, in these cases, the proportion would be still greater except for the preferential action of shearing forces on these relatively large structures. This has been observed on milling natural rubber with chloranil, maleic anhydride, and dithiols, and on milling high molecular-weight GR-S and alfin polybutadiene in nitrogen.

Similar considerations apply to the last class (4) of elastomers, initially cross-linked and cross-linking on mastication. The observable plasticizing and solubilization on mastication with, for example, stored Neoprene, is explicable by the predominance of α over γ. Conversely, increased insolubilization of some GR-S branched copolymers on mastication with a deficiency of "peptizer" (strictly, a radical acceptor) is a case where the value of γ is more important than α.

Chain-length distribution on vulcanization.—In its effect on polymer configuration, vulcanization is a further extension of the cross-linking occurring during polymer formation or mastication. Since normal vulcanizates are cross-linked every few hundred monomer units in chains of several thousand units, the term γ, now representing degree of vulvanization in Equation (5), is much larger than $\alpha + \beta$, representing reciprocal of average chain-length of the cross-linked molecules. The distribution within the vulcanized network is then:

$$N_x/N = \gamma e^{-\gamma x} \tag{6}$$

where N_x is mainly chain-length x between cross-links. Since γ makes other terms unimportant, Equation (6) is then a general distribution function for chain lengths in all vulcanized products. Equation (6) is mathematically identical with Equation (2). A similar physical picture of lengths of chain segments then applies. With the indicated change in ordinates, Figure 5 also represents number and weight fractions at various chain lengths for a vulcanizate.

Subsequent random degradation of the network, as in several types of aging, reintroduces a term α:

$$N_x/N = (\alpha + \gamma)e^{-(\alpha+\gamma)x} \tag{7}$$

where α is now the extent of aging. Equation (7) expresses quantitatively the conclusion that aging by random processes leads to a similar change of properties at the same extent of breakdown, independent of the process or rate of aging. This does not cover the important case of ozone degradation, the effects of which are macroscopic, and not random in the molecular sense required in the above treatment.

Determination α, β, and γ.—In all these equations, which quantitatively describe network structure from the formation of the elastomer to the degradation

of its vulcanizate, there are at most three parameters α, β, and γ requiring evaluation. Determination of these is, therefore, an immediate problem. For linear polymers, β is by definition the reciprocal of the number average chain length. After degradation to an extent α, the number average chain length is now $1/(\alpha + \beta)$. These two quantities can, therefore, readily be determined from number-average molecular weights obtained by osmotic methods. Other average chain length measurements can also yield these quantities, *e.g.*, the weight average chain lengths before and after mastication are $2/\beta$ and $2/(\alpha + \beta)$, and the viscosity averages $1/\beta$. $\Gamma(a + 2)^{1/a}$ and $1/(\alpha + \beta)$. $\Gamma(a + 2)^{1/a}$, respectively, where a is the exponent in the modified Staudinger equation, $\eta = KM^a$.

The determination of quantities, including the extent of cross-linking, γ, has not yet been satisfactorily resolved. There are three types of cross-linking systems for which γ can be determined, (1) when cross-linking is sufficiently low to give a wholly soluble polymer, (2) when sol and gel are both present in measurable amounts, and (3) when the elastomer is almost wholly as an insoluble network. Most attention has been directed, with partial success, to the third type. This includes normal vulcanizates, for which the molecular weight between cross-links, M_c, is equal to m/γ, where m is the molecular weight of the monomeric unit. M_c can, in principle, be determined from stress-strain or swelling properties and, consequently, is subject to the inadequacies of elasticity theory and still awaits a more direct measurement of number of cross-links. The onset and amount of gel has been utilized in the classic work of Flory on polycondensation, and, where applicable, probably gives a more reliable value of γ than is obtained with the complete network. No investigations have been made of completely soluble cross-linked systems. These last seem to offer some simplifications over the other systems in that the fundamental average molecular weights can be determined for the whole system before and after cross-linking.

There is a great need of an absolute standard method of producing a known degree of cross-linking, γ or M_c, in particular for a check and calibration of elasticity measurements. Cross-linking agents, *e.g.*, diazodicarboxylates[16], have been claimed to give quantitative cross-linking, but no satisfactory chemical evidence is yet available. For quantitative cross-linking, peroxide vulcanization appears attractive, both from the chemical viewpoint, and the ready production of cross-linked products of the above three types, enabling several different methods of cross-linking to be applied.

REFERENCES

[1] Gee, *Trans. Faraday Soc.* **36**, 1171 (1940).
[2] Bloomfield, *J. Rubber Research Inst. Malaya* **13**, No. 271.
[3] Baker, *Ind. Eng. Chem.* **41**, 511 (1949).
[4] Morris, unpublished results; see also Bateman, *Trans. Inst. Rubber Ind.* **26**, 246 (1950).
[5] Watson, *Trans. Inst. Rubber Ind.* **29**, 202 (1953).
[6] Flory, *J. Phys. Chem.* **46**, 138 (1942).
[7] Wren, unpublished results; see also Wood, *J. Rubber Research Inst. Malaya* **14**, No. 279.
[8] Wood, *J. Rubber Research Inst. Malaya* **14**, No. 279.
[9] Pike and Watson, *J. Polymer Sci.* **9**, 224 (1952).
[10] Treloar, "The Physics of Rubber Elasticity", Oxford University Press, **1949**.
[11] Farmer and Moore, *J. Chem. Soc.* **1951**, p. 142.
[12] Cunneen, *J. Applied Chem.* **2**, 353 (1952).
[13] Fundamental studies confirm the technological indications that such aging is not analogous chemically to that shown by unsaturated hydrocarbons.
[14] Watson, *Trans. Faraday Soc.* **49**, 842 (1953).
[15] Watson, *Trans. Faraday Soc.* **49**, 1369 (1953).
[16] Flory, Rabjohn, and Shaffer, *J. Polymer Sci.* **4**, 225 (1949).

COPOLYMERIZATION REACTIONS OF CINNAMIC ACID, ITS DERIVATIVES, AND SOME RELATED COMPOUNDS *

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The recent studies[1] which have established the fact that α,β-unsaturated ketones of the benzalacetophenone type copolymerize readily with butadiene have led to a study of derivatives of cinnamic acid. A number of papers and patents cover copolymerization of cinnamaldehyde[2], cinnamic acid[3], cinnamic esters[4], cinnamonitrile and derivatives[5], and esters of β-(α-furyl)-acrylic acid[6] under a variety of conditions, but none of these references give detailed descriptions of the products. Hence a further examination of the copolymerization behavior of these monomers seemed desirable.

Cinnamaldehyde copolymerizes with butadiene in free-radical-initiated emulsion systems using a variety of initiators. In general the copolymer contained a little less cinnamaldehyde than did the monomer mixture used in the preparation. Copolymers of cinnamaldehyde with acrylonitrile and isoprene were readily obtained in the Mutual recipe[7], but no copolymer was obtained with methyl methacrylate or vinyl acetate. In a bulk system, cinnamaldehyde polymerized with methyl vinyl ketone. No homopolymer of the aldehyde could be obtained in a variety of experiments. Copolymers from mixtures containing 90 parts of butadiene and 10 parts of cinnamaldehyde were prepared for evaluation rubbers in the azobisisobutyronitrile-initiated modification of the Mutual recipe at 50° C and in the cumene hydroperoxide recipe at 0° C. The compounded and cured polymers had stress-strain properties much like GR-S and, in addition, had improved low-temperature properties.

Cinnamic acid did not yield a homopolymer in any solution or emulsion system which was tried. It gave copolymers with styrene and butadiene in acid-side emulsion systems initiated by azobisisobutyronitrile. The copolymers produced at 55 to 60 per cent conversion all contained less of the acid than did the monomer mixtures from which they were prepared. The copolymer prepared from 85 parts of butadiene and 15 parts of cinnamic acid was compounded and cured. It had outstanding tensile (up to 5360 pounds per sq. in.) and low-temperature properties (T_{10} — 65° C; T_{100} — 72.5° C; freezing point —72° C), although in temperature-retraction tests it showed a tendency to crystallize. The introduction of the carboxyl group did not have the expected effect of improving the oil resistance of the copolymer[8].

The homopolymerizations of methyl and ethyl cinnamate have been reported[9]. Methyl cinnamate has yielded copolymers with styrene, isoprene,

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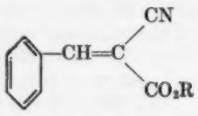
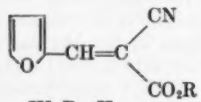
and butadiene in the Mutual recipe, but with acrylonitrile under the same conditions the product appeared, by elemental analysis, to be polyacrylonitrile. Copolymers of butadiene (90 parts) and ethyl cinnamate (10 parts), and methyl cinnamate (10 parts), were evaluated as rubbers. The copolymer of the ethyl ester had stress-strain properties essentially equal to GR-S, as well as excellent low-temperature properties (T_{10} — 62° C; T_{100} — 68° C; freezing point —67.5° C). The hysteresis values were inferior to those of GR-S. The methyl ester copolymer was very similar in properties to the ethyl ester. The hysteresis was slightly better than for the ethyl ester copolymer but still lower than for GR-S.

trans-Cinnamonitrile did not homopolymerize under any conditions tried. It gave a copolymer with methylvinyl ketone in bulk polymerization and it copolymerized with methyl methacrylate, butadiene, and isoprene in the Mutual recipe. A mixture of the *cis*- and *trans*-isomers produced by decarboxylation of α-cyanocinnamic acid[10] did not give satisfactory results in polymerization experiments, and it is believed the *cis*-isomer is an inhibitor. The copolymer from butadiene (90 parts) and *trans*-cinnamonitrile (10 parts) did not equal GR-S in tensile strength or hysteresis. It had rather good low-temperature properties but showed more tendency to crystallize than did GR-S. It was somewhat surprising to find that this nitrile copolymer had poorer oil resistance than GR-S.

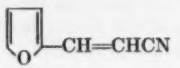
Some preliminary experiments were carried out on the copolymerization of butadiene with ethyl α-cyano-β-phenylacrylate (I), methyl α-cyano-β-phenylacrylate (II), α-cyano-β-phenylacrylic acid (III), α-cyano-β-(α-furyl)-acrylic acid (IV) and its ethyl ester (V), β-(α-furyl)-acrylic acid (VI), ethyl β-(α-furyl)-acrylate (VII), and β-(α-furyl)-acrylonitrile (VIII).



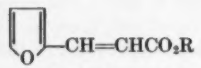
I, R = C_2H_5
II, R = CH_3
III, R = H



IV, R = H
V, R = C_2H_5



VIII



VI, R = H
VII, R = C_2H_5

All of these except (IV) and (V) copolymerized, but none of the polymers seemed to show interesting properties as elastomers. Copolymers also were obtained from (I) with styrene and from (II) with methylvinylketone.

In all of the copolymerizations studied, the entrance of the α,β-unsaturated component into the polymer was established by infrared data on the copolymer.

When the copolymerization was carried out using compounds that contained an element other than carbon, hydrogen, or oxygen, the analysis of the copolymers produced was simple, since ordinary elemental analysis could be used. For example, in copolymers of cinnamonitrile it is only necessary to have a nitrogen analysis to determine the nitrile incorporation in the product. However, because elemental analysis is not sensitive enough for use with other

monomers, the development of an alternative method became necessary. Investigation showed that quantitative ultraviolet absorption analysis was not feasible because the saturated analogs (hydrocinnamaldehyde, hydrocinnamic acid, ethyl hydrocinnamate, and methyl hydrocinnamate) which were used as standards fluoresce, when irradiated with light, in the region where phenyl absorption occurs. A method involving the use of infrared absorption was therefore developed.

All infrared determinations were made on a Perkin-Elmer Model 12-C infrared spectrophotometer, using 1.0-mm. potassium bromide cells at a slit width of 0.062, except that of ethyl α-cyanohydrocinnamate, which was made in a 0.305-mm. sodium chloride cell. The measurements were carried out on the absorption maxima caused by the presence of carbonyl groups, and the saturated analogs of the monomers were used for the standards.

The procedure employed was as follows. A stock solution of from 60 to 80 mg. of the proper standard in 10 cc. of reagent-grade chloroform was prepared. One-cc. portions of this solution were then diluted with varying amounts of chloroform, to make a series of solutions of varying concentrations. The transmittance of these solutions was then determined in the carbonyl region, and the logarithms of those values were plotted against the concentrations in milligrams per milliliter.

The sample for analysis was prepared by covering 0.4000 to 0.6000 gram of the thrice-reprecipitated copolymer with 50 cc. of chloroform (from the same bottle that was used to make up the standard solutions) in a small glass-stoppered flask. This was allowed to stand until solution was complete, about 24 hours, and the transmittance of the solution in the carbonyl region was determined, using the same cell that had been used for the standards. The monomer incorporation was then determined by referring to the calibration curve and dividing the value found by the amount of copolymer placed in solution.

As a typical example, the details of the quantitative infrared analysis for the incorporation of ethyl cinnamate in a series of butadiene-ethyl cinnamate copolymers are given in Tables I and II. In Table I are found the data for the model compound used as the standard, and, Table II the corresponding data for the copolymer.

The absorption of the standard, ethyl hydrocinnamate, followed Beer's law, the graph of log T against concentration being essentially linear. This graph was then used to convert the experimentally observed T values for the copolymer to concentration of the ester moiety, —CH(C$_6$H$_5$)—CH(COOC$_2$H$_5$)— (fourth and fifth

Table I

Quantitative Infrared Absorption Study[a] of Ethyl Hydrocinnamate[b]

Concentration (mg./cc.)	$T = I/I_0$
4.26	0.104
2.84	0.206
2.13	0.248
1.90	0.309
1.42	0.385
0.853	0.497
Pure solvent	0.725

[a] In ester carbonyl region; maximum absorption occurred at 1729 cm.$^{-1}$; cell 1.0 mm.; slit 0.062 mm.
[b] In chloroform solution.

TABLE II

QUANTITATIVE INFRARED ABSORPTION STUDY[a] OF BUTADIENE–ETHYL CINNAMATE COPOLYMERS

Charge ratio, butadiene/ ester	% Conversion	Copolymer concn. (mg./cc.)	$T = I/I_0$	Ester concn., (mg./cc.)	% Ester incorporation
90/10	59.7	10.1	0.517	0.77	7.6
85/15	61.0	10.5	0.436	1.15	12.0
80/20	66.0	7.66	0.454	1.06	15.9

[a] Under identical conditions and with same solvent as in ethyl hydrocinnamate study of Table I.

columns of Table II). The correction factor 176/178, to compensate for the difference in molecular formula between the cinnamate and hydrocinnamate, was less than the infrared precision (±3%), and so was neglected.

Comparison of the charge ratio with the per cent of comonomer incorporation affords information as to the relative rate at which each monomer enters the chain. The incorporation of cinnamaldehyde, cinnamic acid, cinnamonitrile, ethyl cinnamate, and methyl cinnamate was in each case less than the concentration of that particular monomer in the original charge ratio, from which it is concluded that, in these cases, butadiene enters the copolymer chain at a faster rate than the other monomer. The situation is reversed, however, in the case of butadiene-ethyl α-cyano-β-phenylacrylate.

The results of these analyses are listed in Table III.

These data do not permit accurate calculations of reactivity ratios[11], but do indicate little tendency for alternation of monomer units such as occur with maleic anhydride[12], except possibly in the case of ethyl α-cyano-β-phenylacrylate.

EXPERIMENTAL WORK

Materials.—Research grade butadiene[13] was used throughout this work. Acrylonitrile, cinnamaldehyde, cinnamic acid, ethyl cinnamate, methyl cinna-

TABLE III

COMONOMER INCORPORATION IN COPOLYMERS WITH BUTADIENE

Nonbutadiene monomer, X	Charge ratio, butadiene/ X	% Conversion	Absorption maxima, ($cm.^{-1}$)	% Incorporation of X
Cinnamaldehyde	90/10	52.8	1729	7.1
	85/15	65.6	1729	9.6
	80/20	65.6	1729	13.4
Cinnamic acid	90/10	56.9	1715	9.2
	85/15	61.5	1715	9.6
	80/20	58.7	1715	10.5
Cinnamonitrile	90/10	60.0	—	8.26[a]
	85/15	54.0	—	8.45[a]
	80/20	53.0	—	9.41[a]
Ethyl cinnamate	90/10	59.7	1729	7.6
	85/15	61.0	1729	12.0
	80/20	66.0	1729	15.9
Methyl cinnamate	90/10	50.2	1736	7.5
	85/15	50.0	1736	9.1
	80/20	56.5	1736	12.1
Ethyl α-cyano-β-phenylacrylate	90/10	41.2	—	24.3[a]

[a] Calculated from nitrogen analyses.

mate, isoprene, methyl methacrylate, styrene, vinyl acetate, and azobisisobutyronitrile were obtained on the market and carefully purified before use. *trans*-Cinnamonitrile was prepared by the method of Plaut and Ritter[14] and the portions used boiled at 94–97° C (0.4 mm.); n_D^{20} 1.6031. α-Cyano-β-phenylacrylic acid, melting at 180° C, was prepared by a method described[15]. α-Cyano-β-(α-furyl)-acrylic acid, melting at 218° C, was prepared in 84.1 per cent yield by a strictly analogous method. Ethyl α-cyano-β-(α-furyl)-acrylate, melting point 92° C, was prepared by the method of Bechert[16]. Ethyl β-(α-furyl)-acrylate, melting point 24° C, was prepared by the method of Posner[17]. Ethyl α-cyano-β-phenylacrylate, melting point 49.9° C, was prepared by published directions[18]. Ethyl and methyl hydrocinnamates were prepared by the procedure of Erlenmeyer[19]. Methyl α-cyano-β-phenylacrylate, melting point 87–89° C, was prepared by the method of Carrick[20]. Ethyl α-cyanohydrocinnamate was prepared by the reduction with hydrogen, in the usual manner, of 20.1 grams of ethyl α-cyano-β-phenylacrylate in 100 cc. of 95% ethanol over 0.20 gram of platinum oxide catalyst at room temperature at a pressure not exceeding 50 pounds per sq. inch. The product boiled at 132° C (1.2 mm.); n_D^{20} 1.5108; yield 16.8 grams.

ANALYSIS. Calculated for $C_{12}H_{11}O_2N$. C, 70.94; H, 6.45
FOUND. C, 71.54; H, 6.29

TABLE IV

COPOLYMERIZATION OF BUTADIENE AND CINNAMALDEHYDE

Charging ratio	Initiator (g.)	Modifier (g.)	Temp. (° C)	Time (hours)	Conversion (%)	Benzene solubility (%)	Inherent viscosity
A. Mutual recipe with potassium persulfate initiation							
95/5	0.060	0.050	30	94	60	73	4.6
95/5	0.060	0.050	30	51	47	100	2.6
95/5	0.060	0.050	50	24	85	Insol.	—
90/10	0.060	0.050	30	53	24	100	1.4
90/10	0.060	0.050	50	21	60	100	3.6
85/15	0.060	0.050	50	16	50	87	2.9
80/20	0.060	0.050	50	17	48	80	2.3
75/25	0.060	0.050	50	17	47	71	2.7
70/30	0.060	0.050	50	16	53	80	3.0
B. Mutual recipe with azobisisobutyronitrile initiation							
90/10	0.02	0.050	50	18	91	Insol.	—
90/10	0.01	0.050	50	16	60	91	3.2
90/10	0.01	0.075	50	18	53	95	1.8
90/10	0.01	0.100	50	18	59	91	1.7
85/15	0.01	0.075	50	17	38	92	1.8
85/15	0.02	0.125	50	15	54	90	0.9
85/15	0.03	0.125	50	15	60	87	1.6
80/20	0.01	0.075	50	17	39	93	2.5
80/20	0.03	0.125	50	15	65	84	2.0
C. Cumene hydroperoxide recipe							
90/10	0.04	0.050	0	15	50	88	3.0
90/10	0.04	0.100	0	19	52	93	3.2
90/10	0.04	0.150	0	24	60	93	2.2
90/10	0.04	0.200	0	24	44	97	0.7
85/15	0.04	0.150	0	30	46	96	2.4
80/20	0.04	0.125	0	24	67	91	3.5

TABLE V

COPOLYMERIZATION OF BUTADIENE AND CINNAMIC ACID
(Acid-side recipe with azobisisobutyronitrile initiation at 50° C)

Charging ratio	Initiator (g.)	Modifier (g.)	Time (hours)	Conversion (%)	Benzene solubility (%)	Inherent viscosity
90/10	0.01	0.050	16	47	99	1.4
90/10	0.02	0.025	15	61	48	2.4
90/10	0.02	0.050	15	54	100	1.5
85/15	0.03	0.050	15	75	100	1.6
80/20	0.02	0.050	15	57	100	1.8
80/20	0.03	0.050	15	65	100	1.1

Polymerization Recipes.—The Mutual recipe[7], the azobisisobutyronitrile-initiated Mutual recipe[1], and the 0° C cumene hydroperoxide recipe[21] were used as described before.

An azobisisobutyronitrile-initiated acid-side recipe of the following type[22] was employed in the copolymerization of cinnamic acid and the other unsaturated organic acids employed in this work with butadiene.

Monomers (total) (grams)	20.0
Azobisisobutyronitrile (gram)	0.02 to 0.06
Water (boiled to remove oxygen) (cc.)	38
MP-635-S (a sodium C_{16} alkanesulfonate mixture) (cc.)	2.0
Technical dodecanethiol (gram)	0.025 to 0.100

TABLE VI

COPOLYMERIZATION OF BUTADIENE AND *trans*-CINNAMONITRILE

Charging ratio	Initiator (g.)	Modifier (g.)	Temp. (° C)	Time (hours)	Conversion (%)	Benzene solubility (%)	Inherent viscosity
A. Mutual recipe with potassium persulfate initiation							
95/5	0.060	0.050	30	47	12	100	1.2
95/5	0.060	0.050	30	72	40	100	1.6
90/10	0.060	0.050	50	22	80	Insol.	—
85/15	0.060	0.050	50	24	67	94	2.1
80/20	0.060	0.050	50	24	61	81	2.5
75/25	0.060	0.050	30	72	59	68	1.8
70/30	0.060	0.050	30	90	67	70	2.0
B. Mutual recipe with azobisisobutyronitrile initiation							
90/10	0.02	0.050	50	13	51	95	1.6
90/10	0.04	0.050	50	13	63	96	2.6
85/15	0.04	0.025	50	12	50	87	2.6
85/15	0.04	0.050	50	12	60	97	2.2
80/20	0.04	0.050	50	12	61	89	1.7
80/20	0.04	0.025	50	12	54	89	3.9
C. Cumene hydroperoxide recipe							
90/10	0.04	0.025	0	12	60	97	3.4
90/10	0.04	0.075	0	12	66	96	3.5
90/10	0.04	0.150	0	8	56	90	1.8
85/15	0.04	0.025	0	8	59	90	2.1
85/15	0.04	0.075	0	8	63	86	1.6
80/20	0.04	0.025	0	8	63	96	1.8

Butadiene Copolymers.—The copolymerizations with butadiene of the various α,β-unsaturated compounds were carried out in the standard manner and the polymerizations and products are listed in Tables IV to IX. In each of these tables the charging ratio is the weight ratio of reactants, butadiene to comonomer; the initiator is specified in the recipe and the modifier is technical dodecanethiol; temperature and time refer to the polymerization process; conversion is the yield of copolymer; and solubility and viscosity are those of the copolymer.

The copolymers of butadiene and cinnamaldehyde listed in Table IV were examined in the infrared and all showed the carbonyl band characteristic of the aldehyde group at 1729 cm.$^{-1}$.

Infrared showed absorption at 1700 cm.$^{-1}$ characteristic of the carboxyl group, which confirmed the presence of the cinnamic acid in the copolymer (Table V).

The copolymers prepared with *trans*-cinnamonitrile showed absorption at 2248 cm.$^{-1}$, confirming the presence of the nitrile group (Table VI).

The ethyl cinnamate copolymers showed absorption bands at 1736 cm.$^{-1}$ characteristic of the ester carbonyl group (Table VII).

TABLE VII

COPOLYMERIZATION OF BUTADIENE AND ETHYL CINNAMATE

Charging ratio	Initiator (g.)	Modifier (g.)	Temp. (° C)	Time (hours)	Conversion (%)	Benzene solubility (%)	Inherent viscosity
A. Mutual recipe with potassium persulfate initiation							
95/5	0.060	0.050	30	94	80	67	2.0
90/10	0.060	0.050	30	50	76	98	2.6
85/15	0.060	0.050	30	48	60	86	1.4
80/20	0.060	0.050	30	49	72	90	2.2
75/25	0.060	0.050	30	49	76	76	1.8
70/30	0.060	0.050	30	64	90	80	2.0
B. Mutual recipe with azobisisobutyronitrile initiation							
90/10	0.01	0.050	50	15	69	94	2.7
90/10	0.02	0.025	50	12	62	97	3.5
90/10	0.04	0.025	50	10	62	100	3.1
85/15	0.02	0.025	50	12	62	99	3.2
80/20	0.02	0.025	50	10	66	100	2.6
C. Cumene hydroperoxide recipe							
90/10	0.04	0.025	0	8	57	91	4.0
90/10	0.04	0.050	0	8	58	97	3.3
90/10	0.04	0.125	0	6	47	88	3.0
90/10	0.04	0.200	0	6	59	99	1.7
85/15	0.04	0.175	0	6	65	97	1.9
80/20	0.04	0.075	0	4.5	54	85	2.6
80/20	0.04	0.125	0	5	73	95	1.7

The methyl cinnamate copolymers showed absorption at 1733 cm.$^{-1}$, which is characteristic of the ester group in the saturated model compound (Table VIII).

TABLE VIII

COPOLYMERIZATION OF BUTADIENE AND METHYL CINNAMATE

Charging ratio	Initiator (g.)	Modifier (g.)	Temp. (° C)	Time (hours)	Conversion (%)	Benzene solubility (%)	Inherent viscosity
A. Mutual recipe with potassium persulfate initiation							
95/5	0.060	0.050	30	72	75	90	2.1
90/10	0.060	0.050	30	50	60	100	2.4
85/15	0.060	0.050	30	48	53	82	1.4
70/30	0.060	0.050	30	57	81	76	1.8
B. Mutual recipe with azobisisobutyronitrile initiation							
90/10	0.02	0.025	50	10	56	97	2.3
85/15	0.02	0.025	50	11	65	90	3.7
85/15	0.02	0.050	50	10	63	92	1.6
80/20	0.02	0.025	50	10	66	92	3.3
C. Cumene hydroperoxide recipe							
90/10	0.04	0.050	0	4	47	94	3.2
90/10	0.04	0.100	0	4	48	95	2.4
85/15	0.04	0.100	0	8	63	94	3.5
85/15	0.04	0.200	0	5	67	95	2.0
80/20	0.04	0.125	0	8	65	97	3.2

These copolymers gave characteristic carbonyl absorption at 1738 cm.$^{-1}$ and nitrile absorption at 2240 cm.$^{-1}$ (Table IX).

EVALUATION OF BUTADIENE COPOLYMERS AS RUBBERS

Large samples (250 grams or more) of copolymers of butadiene with cinnamaldehyde, cinnamic acid, cinnamonitrile, ethyl cinnamate, and methyl cinnamate have been evaluated as rubbers. They were cured in the tread-stock recipe and carcass-stock recipe listed below, and the stress-strain, low-tempera-

TABLE IX

COPOLYMERIZATION OF BUTADIENE AND ETHYL α-CYANO-β-PHENYLACRYLATE

Charging ratio	Initiator (g.)	Modifier (g.)	Temp. (° C)	Time (hours)	Conversion (%)	Benzene solubility (%)	Inherent viscosity
A. Mutual recipe with potassium persulfate initiation							
95/5	0.060	0.050	30	54	52	100	1.9
90/10	0.060	0.050	30	50	37	100	1.3
85/15	0.060	0.050	30	72	47	93	1.0
80/20	0.060	0.050	30	72	52	82	1.3
75/25	0.060	0.050	30	72	44	89	1.2
75/25	0.060	0.050	50	15	58	88	3.0
B. Mutual recipe with azobisisobutyronitrile initiation							
90/10	0.01	0.025	50	21	75	100	1.6
90/10	0.01	0.050	50	17	48	93	1.9

TABLE X

MISCELLANEOUS COPOLYMERIZATIONS

Monomer A	Monomer B	A/B (g.)	Recipe	Temp. (° C.)	Time (hours)	Conversion (%)	Infrared band (cm.$^{-1}$) for characterization
Butadiene	β-(α-Furyl)-acrylic acid	18/2	1	50	17	24	1702 carbonyl
Butadiene	Ethyl β-(α-furyl)-acrylate	18/2	2	50	24	51[a]	1736 carbonyl
Butadiene	β-(α-Furyl)-acrylonitrile	19/1	3	30	116	14[b]	2240 nitrile
Acrylonitrile	Cinnamaldehyde	18/2	4	50	24	25	1608 phenyl
Isoprene	Cinnamaldehyde	18/2	4	50	16	82	1718 aldehyde
Methyl methacrylate	Cinnamaldehyde	18/2	4	50	16	[c]	1718 aldehyde
Vinyl acetate	Cinnamaldehyde	18/2	4	50	24	0	1718 aldehyde
Methylvinyl ketone[d]	Cinnamaldehyde	24/3	5	50	7	100	1700 carbonyl
Styrene	Cinnamic acid	18/2	1	50	24	100	1740 carbonyl
Isoprene	*trans*-Cinnamonitrile	18/2	4	50	16	81	2240 nitrile
Methyl methacrylate	*trans*-Cinnamonitrile	18/2	4	50	24	100	2248 nitrile
Methylvinyl ketone[d]	*trans*-Cinnamonitrile	25/2	5	50	7	100	2240 nitrile
Acrylonitrile	*trans*-Cinnamonitrile	18/2	4	50	24	0	
Vinyl acetate	*trans*-Cinnamonitrile	18/2	4	50	24	0	1736 carbonyl
Isoprene	Methyl cinnamate	18/2	4	50	16	68	1736 carbonyl
Styrene	Methyl cinnamate	18/2	4	50	7	100	1722 carbonyl
Acrylonitrile	Methyl cinnamate	18/2	4	50	24	40[e]	1740 carbonyl
Butadiene	α-Cyano-β-phenylacrylic acid	18/2	1	50	17	35	2150 nitrile
Butadiene	Methyl α-cyano-β-phenylacrylate	18/2	4	30	54	65[f]	1747 carbonyl
Methylvinyl ketone[d]	Methyl α-cyano-β-phenylacrylate	25/2	5	50	7	100	2248 nitrile
Methyl methacrylate	Ethyl α-cyano-β-phenylacrylate	18/2	4	50	19	100	2248 nitrile
Styrene	Ethyl α-cyano-β-phenylacrylate	18/2	4	50	19	100	1738 carbonyl

Recipe 1. Acid-side recipe with azobisisobutyronitrile initiation.
Recipe 2. Mutual recipe with azobisisobutyronitrile initiation.
Recipe 3. Marvel-Meinhardt acid-side recipe[14].
Recipe 4. Mutual recipe with persulfate initiation.
Recipe 5. Bulk system with benzoyl peroxide initiation.

[a] This copolymer was 91% soluble in benzene and had an inherent viscosity of 2.6.
[b] This copolymer was 90% soluble in benzene and had an inherent viscosity of 2.3.
[c] Analysis showed that the polymer was polymethyl methacrylate.
[d] An 85% methylvinyl ketone–15% water azeotrope.
[e] Analysis indicated this polymer was polyacrylonitrile.
[f] This copolymer was 93% soluble in benzene and had an inherent viscosity of 1.7.

TABLE XI

EVALUATION SAMPLES

Sample No.	X-603	X-672	XP-99	1Z Bld. 20	258	273	274	277	252	253
Comonomer with butadiene	Styrene	Styrene	Styrene	None	Cinnamaldehyde	Cinnamaldehyde	Cinnamic acid	Cinnamonitrile	Ethyl cinnamate	Methyl cinnamate
Ratio, butadiene to comonomer	71.5/28.5	75/25	72/29	100/0	90/10	90/10	85/15	90/10	90/10	90/10
Gel (%)	2	—	—	—	—	2	28	5	5	8
Dilute solution viscosity	2.4	—	—	—	3.5	2.7	1.25	3.76	2.2	2.7
Conversion (%)	—	—	63	69.9	54	60	59	59	53	49
Mooney viscosity (ML-4)	53	—	155	29	122.5	137	123	119	45	79
Temperature of polymerization (° C)	47	5	5	50	50	0	50	50	30	30
Recipe used	Mutual	Mutual	*p*-Tolyldiazothio-*β*-naphthyl ether	Mutual	Mutual	Cumene hydroperoxide	Acid-side azobisisobutyronitrile	Mutual	Mutual	Mutual

ture, oil-resistance, and hysteresis properties were determined by standard testing procedures[23].

Tread stock recipe		Carcass stock recipe	
Polymer	60	Polymer	100
EPC black	24	Statex 93	30
Zinc oxide	3	Red lead	2.5
Sulfur	1.2	Circosol 2×H	20
Altax	1.05	Sulfur	2
		Altax	1

The cinnamaldehyde-butadiene copolymer prepared in the Mutual recipe (azobisisobutyronitrile initiated) showed a somewhat low tensile strength in the tread-type recipe. Its low-temperature properties were very good but its oil resistance was no better than that of GR-S. The sample prepared in the cumene hydroperoxide recipe had a high Mooney viscosity. It showed good low-temperature properties and not too much tendency to crystallize, but its oil resistance was poor. The hysteresis values were not improved over those of high-viscosity GR-S.

The cinnamic acid-butadiene copolymer had outstandingly good tensile strength and low-temperature properties. However, the temperature-retraction tests showed a tendency toward crystallization. Its oil resistance was rather poor and the hysteresis values were slightly lower than those of standard GR-S.

The cinnamonitrile-butadiene copolymer (Mutual recipe, azobisisobutyronitrile initiated) had a relatively high Mooney viscosity. Its low-temperature properties were good, but it showed a tendency toward crystallization. Its oil resistance was poor and its hysteresis values were slightly lower than those of standard GR-S.

TABLE XII

STRESS-STRAIN DATA AT 77° F.
(Tread-type recipe)

	Min. cured at 292° F	Sample No.							
		X-603	1Z Bld. 20	258	273	274	277	252	253
300% modulus (lb./sq. in.)	25	650	360	1140	1466	1820	990	600	710
	50	1500	530	—	1800	2110	1450	1130	1170
	75	1940	770	—	2050	2460	1570	1310	1220
	100	2210	790	—	2000	2400	1580	1340	1350
	150	2390	1000	—	1910	2640	—	1420	1390
Tensile strength (lb./sq. in.)	25	2090	460	1050	2550	5360	1310	3760	3560
	50	3919	1020	1380	2350	5370	2160	3090	3620
	75	3770	1430	—	2390	4910	2030	3070	2960
	100	2670	1420	1350	2370	5010	2090	2470	3280
	150	3010	1640	—	2120	3690	1350	2930	3410
Elongation (%)	25	650	400	290	430	370	350	830	740
	50	560	480	270	360	360	380	550	590
	75	460	440	—	320	300	360	510	490
	100	350	440	270	340	310	350	430	510
	150	340	410	—	320	240	350	460	510
Set (%)	25	13	6	7	8	2	7	18	14
	50	13	7	5	5	3	9	10	10
	75	9	6	—	4	1	7	6	6
	100	4	6	5	4	3	6	5	6
	150	4	5	—	4	1	4	6	7

TABLE XIII

GEHMAN LOW-TEMPERATURE DATA

(Tread-type recipe)

	Sample No.								
	X-603	1Z Bld. 20	X-672	258	273	274	277	252	253
	Minutes cured at 292° F								
	—	—	50	50	—	—	—	60	60
Temp. (−° C)	Degrees twist 10 seconds after twist								
80		5						2	2
75		15		3	3	4	4	2	2
70		109		18	7	17	8.5	2	3.5
65		134		99	34	58	51	25	23
60	3	148		120	104	103	103	73	84
55	5	152	4	127	118	125	124	96	103
50	24	157	21	133	114	130	132	110	114
45	94	161	68	135	112	131	136	118	120
40	127		98	139	115	132	141	123	125
35	138		114	139	121	133	143	128	131
30	144		123	141	128	133	147	132	133
25	149		129	—	133	133	—	—	138
20	—		134	—	144	133	—	—	—
15				—	152	134	—		
10				—	—	135	—		
5				—	—		—		
0	159	171	146	151	156	142	156	144	146
−25	162	173	151	154	157	150	159	147	150
	Temperature (−° C)								
T_2[a]	27.5	28.0	24	47	23.0	52.5	38	39.5	38
T_5[a]	42.5	57.5	41	65	60.0	61.5	59	57.5	58.5
T_{10}[a]	45.5	67.0	45.5	67	62.0	65.0	62	62	63
T_{100}[a]	51.5	74.0	53	72	68.5	72.5	69	68	67.5
F.P.	52.0	76.0	52	71	67.5	72.0	70	67.5	67
	Gage of sample (inch)								
	0.082	0.070	0.078	0.096	0.083	0.091	0.094	0.083	0.081
	Temperature retraction test[b], Sample No.								
	X-603	XP-169[c]	1Z Bld. 20	Natural rubber	258	273	274	277	252	253
	Minutes cured at 292° F									
	60	40	60	60[d]	50	50	50	50	40	40
% Retraction	Temperature (−° C)									
5	53		76		73	60	73	70		
10	51	53	74	64.5	71	51	71	69	70	69
20	48		69		67	36	67	64		
30	44	32.5	62	56.5	63	31	63	60	67	66
40	40		57		59	27	53	55		
50	36	19	51	49.5	53	22	32	50	58	59
60	31		46		49	18	23	43		
70	25	12	39	35	42	14	17	37	43	45
80	14		33		35	8	9	29		
90	+4		19		21	+13	+1	14		
(TR_{-10}) minus (TR_{-70})	26	41	35	29.5	29	37	54	32	27	24

[a] T_2, T_5, T_{10}, T_{100} values are temperatures at which relative rotation stiffness is 2, 5, 10, 100.

[b] T_{50} samples 2 inches long, elongation 100%. Samples conditioned at −80° C for 30 minutes before testing. Temperature raised 1° C per minute.

[c] Polybutadiene made at 14° F.

[d] Cured at 280° F.

TABLE XIV

OIL RESISTANCE
(Tread recipe)

	Sample No.							
	X-603	Perbunan 18	258	273	274	277	252	253
	7-Day immersion, minutes cured at 292° F							
	60		50	50	50	50	60	60
	% volume increase at 77° F							
No. 1 oil	9	0	16	23	16	16	23	19
No. 2 oil	26	6	41	44	37	37	44	41
No. 3 oil	100	19	110	110	100	120	125	120
100% iso-octane	56	13	64	73	69	60	77	77
60/40 iso-octane/ toluene	174	82	152	157	192	152	192	199
Special solvent mixture	174	77	146	163	180	163	186	199

TABLE XV

CARCASS-TYPE RECIPE

		Sample No.									
Stress-strain at 77° F.	Min. cured at 280° F	X-603	XP-99	X-672	1Z Bld. 20	258	273	274	277	252	253
300% modulus (lb./sq. in.)	20	160	—	—	430	850	620	—	460[a]	380	400
	30	310	—	—	580	1080	800	610	580[a]	500	590
	40	470	—	—	—	—	920	850	630[a]	550	680
	60	710	—	—	—	—	920	1050	720[a]	630	820
	80	700	—	—	—	—	1010	1130	730[a]	700	890
Tensile strength (lb./sq. in.)	20	1790	—	—	610	1230	1590	—	1410	1220	1300
	30	2090	—	—	590	1140	1350	2440	1120	1200	1110
	40	2190	—	—	590	1090	1230	1910	1170	930	1110
	60	1350	—	—	530	970	990	1370	1280	850	930
	80	1470	—	—	440	980	1230	1330	1120	830	860
Elongation (%)	20	990	—	—	380	370	510	—	380	590	560
	30	780	—	—	300	310	400	620	290	510	450
	40	670	—	—	290	280	360	470	260	410	400
	60	470	—	—	250	260	310	350	280	360	340
	80	480	—	—	240	260	350	330	260	340	300
Set (%)	20	37	—	—	2	2	3	—	2	5	4
	30	28	—	—	1	1	1	4	1	3	1
	40	21	—	—	0	0	2	2	1	1	0
	60	6	—	—	0	0	1	1	1	2	0
	80	5	—	—	0	0	0	0	1	1	0
	Goodrich Hysteresis Data										
Shore hardness	30	—	50	41	42	53	51	50	50	43	46
	60	42	51	42	42	55	51	51	54	46	49
	90	41	51	42	41	55	54	54	55	46	51
	120	41	—	—	—	—	—	—	—	—	—
Initial compression (%)	30	—	25.6	36.5	30	19.4	21.6	27.9	21.5	28.5	25.8
	60	32.8	20.7	30.7	27.1	18.5	20.4	20.7	19.0	27.5	22.7
	90	31.6	21.2	30.6	27.6	17.5	17.5	20.8	18.5	23.7	21.9
	120	31.1	—	—	—	—	—	—	—	—	—
Heat rise (° F)	30	—	17	41	27	13	16	30	21	27	19
	60	26	11	24	15	11	11	15	16	23	13
	90	22	9	20	18	11	8	14	15	15	13
	120	20	—	—	—	—	—	—	—	—	—
Set (%)	30	—	11.4	31.2	18.0	4.9	5.9	21.5	6.8	14.5	10.8
	60	16.0	2.4	10.2	4.7	1.2	1.7	4.2	2.5	6.5	3.5
	90	8.6	1.6	6.3	3.2	1.0	0.3	2.7	1.6	3.6	1.5
	120	5.3	—	—	—	—	—	—	—	—	—

[a] 200% modulus.

The ethyl cinnamate-butadiene copolymer had stress-strain values about equal to those of GR-S. Its low-temperature properties were excellent, its oil resistance was poor, and its hysteresis properties were slightly better than those of standard GR-S.

The methyl cinnamate-butadiene copolymer was similar to the copolymer prepared with ethyl cinnamate. Its hystersis values, however, were better than those of the latter, but still inferior to those of high-viscosity GR-S.

SUMMARY

A study of the copolymerization of butadiene with cinnamaldehyde, cinnamic acid, methyl cinnamate, ethyl cinnamate, and *trans*-cinnamonitrile showed that all these monomers yield rubbery copolymers with butadiene and certain of these have been evaluated and compared to current synthetic rubbers of the GR-S type. In general, these monomers to the extent of 10 to 90 parts of butadiene yield copolymers roughly equivalent to the standard GR-S which contains approximately 25 parts of styrene. The cinnamic acid-butadiene copolymer has excellent tensile strength. The *trans*-cinnamonitrile copolymer shows no improvement in oil resistance over GR-S. These cinnamic acid derivatives all enter the growing butadiene copolymer chain somewhat more slowly than does butadiene, so that the copolymers contain a lower percentage of the comonomer than does the charging stock used.

Some experiments were conducted on the copolymerization of these cinnamic acid derivatives with other monomers than butadiene, the copolymerization of the furan analogs of the cinnamic acid derivatives, and the copolymerization of α-cyano-β-phenylacrylic acid derivatives.

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The Micro-Tech Laboratories, Skokie, Ill., performed the microanalyses reported.

The authors are indebted to Stanley Detrick, E. I. du Pont de Nemours & Co., for the MP-635-S used as an emulsifier in the acid-side recipes. This emulsifier had the following percentage composition:

Sodium alkanesulfonates, approximately C_{14}	49.5
Unreacted hydrocarbons	10.3
Sodium chloride	0.86
Sodium sulfate	0.4
Balance water, and about 3% isopropyl alcohol	

REFERENCES

[1] Marvel, Peterson, Inskip, Taft, and Labbe, *Ind. Eng. Chem.* **45**, 1532 (1953).
[2] Marvel and Wright, *J. Polymer Sci.* **8**, 495 (1952).
[3] Stoesser and Lowery, U. S. patent 2,232,930 (Feb. 25, 1941); Bobalek, U. S. patents 2,470,752 and 2,470,757 (May 24, 1949).

[6] I. G. Farbenindustrie A.-G., British patent 368,567 (Mar. 10, 1932); Carpmael and I. G. Farbenindustrie A.-G., British patent 387,381 (Feb. 6, 1933); E. I. du Pont de Nemours & Co., British patent 494,752 (Oct. 25, 1938); Britton, Marshall, and LeFevre, U. S. patent 2,341,175 (Feb. 8, 1944); Swart, U. S. patent 2,594,824 (Apr. 29, 1952); Bartlett, U. S. patent 2,612,475 (Sept. 30, 1952).
[7] Seymour, U. S. patent 2,465,318 (Mar. 22, 1949); Emerson, U. S. patent 2,498,616 (Feb. 21, 1950); Swart, U. S. patent 2,594,824 (Apr. 29, 1952).
[8] Blicke, *Ber.* **47**, 1352 (1914); Habgood, Hill, Isaacs, and Morgan, U. S. patent 2,231,623 (Feb. 11, 1941); Gavatin, Swedish patent 121,341 (Apr. 6, 1948).
[9] Frank, Adams, Biegen, Deanin, and Smith, *Ind. Eng. Chem.* **39**, 887 (1947).
[10] Marvel, Fukuto, Berry, Taft, and Labbe, *J. Polymer Sci.* **8**, 599 (1952).
[11] Marvel and McCain, *J. Am. Chem. Soc.* **75**, 3272 (1953).
[12] Gohsez, *Bull. soc. chim. belg.* **41**, 477 (1932).
[13] Mayo and Walling, *Chem. Revs.* **46**, 191 (1950).
[14] Wagner-Jauregg, *Ber.* **63**, 3213 (1930).
[15] The research grade of the Phillips Petroleum Company was used.
[16] Plaut and Ritter, *J. Am. Chem. Soc.* **73**, 4076 (1951).
[17] Lapworth and Baker, in "Organic Syntheses", John Wiley & Sons, New York, 2nd Ed., 1941, Vol. 1, p. 181.
[18] Bechert, *J. prakt. Chem.* **50**, (2), 1 (1894).
[19] Posner, *J. prakt. Chem.* **82**, (2), 425 (1910).
[20] Inglis, in "Organic Syntheses", John Wiley & Sons, New York, 2nd Ed., 1941, Vol. 1, p. 254.
[21] Erlenmeyer, *Ann.* **127**, 334 (1866).
[22] Carrick, *J. prakt. Chem.* **45**, (2), 501 (1892).
[23] Marvel, Menikheim, Inskip, Taft, and Labbe, *J. Polymer Sci.* **10**, 39 (1953).
[24] This recipe was developed by Richard M. Potts.
[25] Garvey, American Society for Testing Materials, D471-43T; Gehman, Woodford, and Wilkinson, *Ind. Eng. Chem.* **39**, 1108 (1947); R. T. Vanderbilt Co., "Vanderbilt Handbook", New York, 9th Ed., 1948, p. 65.
[26] Marvel and Meinhardt, *J. Polymer Sci.* **6**, 733 (1951).

INFRARED EXAMINATION OF VARIOUS POLYISOPRENES *

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INTRODUCTION

It is well known that, in general, the laboratory polymerization of diene monomers leads to materials which are intramolecular mixtures of various types of addition products. Thus, synthetic polyisoprene has been shown to contain chemical groupings arising from 1,2, 3,4, and 1,4 addition of the isoprene units[1]. This is in contrast to the naturally occurring high polymers of isoprene, the rubbers and guttas, which appear to be exclusively *cis*-1,4 and *trans*-1,4 adducts, respectively[2]. An exception to this last statement is the polyisoprene derived from chicle, which is a mixture of *cis*-1,4 and *trans*-1,4 addition[3]. In this case, however, the mixture is an intermolecular one, and fractionation of the material leads to components which are all *cis*-1,4 and all *trans*-1,4.

The general problem of diene polymerization is, of course, of great importance, and the synthetic polyisoprenes are of particular interest because of their relationship to natural rubber. The following attempt to obtain a quantitative analysis for the various types of addition occurring in synthetic polyisoprenes may lead to a better understanding of the nature of these materials and may be of help in elucidating the effect of microstructure on rheological properties.

The various structures arising from the linear polymerization of isoprene are shown in Figure 1. Addition across the 1,4 positions of the isoprene monomer leads to carbon-carbon double bonds which are part of the polymer chain

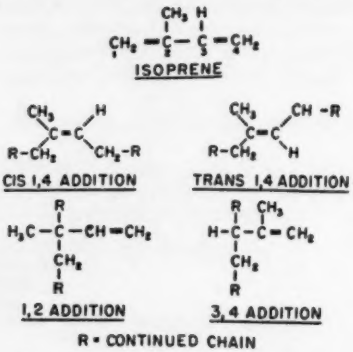

FIG. 1.—Linear polymerization of isoprene.

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(internal double bonds), and these may have the chain continued in either the *cis* or *trans* configuration. Addition across the 1,2 or 3,4 positions leads to vinyl or isopropenyl side groups (external double bonds), respectively. The analysis given below is a determination of the concentrations of these various types of double bonds in the polymer chains. In addition to the structures shown in Figure 1, there exists the possibility of other groupings, such as cyclic structures and various linkages arising from chain transfer reactions during the course of polymerization. While none of these latter structures has been taken into account here, there is evidence from the analyses given below that some cationic polymers contain a rather high incidence of structures other than those shown in Figure 1. Finally it should be noted that, as long as such extraneous structures do not involve loss of double bonds and do not show interfering absorptions, they will not be detected here.

Qualitative examinations of the infrared spectra of various polyisoprenes have been made by Field, Woodford, and Gehman[4], Dinsmore and Smith[5], Saunders and Smith[6], and others. The general features of polyisoprene spectra in the rock salt region are shown in Figure 2, where the spectra of Hevea (*cis*-1,4), gutta-percha (*trans*-1,4) in the amorphous and α and β crystalline forms, and synthetic polyisoprene prepared with free radical, alfin, and sodium catalysts are given. The assignment of the strong bands as marked on the spectrograms is quite unambiguous. The assignments are made only to certain specific chemical groupings, and no attempt has been made here to assign the weaker bands. It is seen that, in the region of frequency higher than 950 cm.$^{-1}$, the only outstanding differences among the polymers is the doubling of the carbon-carbon double bond stretching modes at about 1650 cm.$^{-1}$ in the synthetic polyisoprenes. Examination of the carbon-hydrogen stretching modes in the 3000 cm.$^{-1}$ region and the methylene and methyl bands at about 1450 and 1380 cm.$^{-1}$ under higher resolution (CaF_2 prism) indicates that there are small differences among the polymers, but none great enough to be useful for analytical purposes. The region between 700 cm.$^{-1}$ and 950 cm.$^{-1}$ shows the greatest differences. Here the *cis*-1,4 rubber (Hevea) shows a single medium strong band at about 840 cm.$^{-1}$. The *trans*-1,4 gutta shows a variety of bands, depending on its physical state (α or β crystalline form or amorphous), but, when amorphous, shows a fairly strong band also at about 840 cm.$^{-1}$. The synthetic polyisoprene also shows the 840 cm.$^{-1}$ band which very apparently arises from the 1,4 linkages in this polymer. In addition, there are bands at 909 and 887 cm.$^{-1}$ in this material. By comparison with the spectra of a large number of olefinic compounds, these two bands can be assigned respectively to the vinyl and isopropenyl groups arising from 1,2 and 3,4 addition. With this admittedly rather limited understanding of the spectra it is possible to develop an analysis for the various structures in the synthetic polymers.

METHOD OF INFRARED ANALYSIS

The basic assumption of any optical analysis is, of course, the validity of the Beer-Lambert law:

$$d_\nu/l = \sum_{i=1}^{n} \alpha_{\nu i} c_i \qquad (1)$$

where d_ν/l is the optical density per unit path length at frequency ν, $\alpha_{\nu i}$ is the extinction coefficient at this frequency, c_i the concentration of the ith component, and the summation is carried out over the n components of the mixture.

In dealing with a mixture whose components are not available in the pure state, one must resort to the use of some selected model compounds and assume that the α_ν's can be carried over from these models to the system under investigation. In the case of intramolecular mixtures, there is the additional assumption that the extinction coefficients obtained are independent of the nature and proximity of the other substituents in the molecule as well as their concentrations.

The question now arises as to how accurately such extinction coefficients can be carried over from one molecule to another. If one considers the spectra of a series of molecules all containing some particular chemical grouping, one generally finds at least one absorption frequency which is characteristic of the group. If this frequency is constant for the series, it is because the vibration involves primarily motion of the atoms within the grouping; and the actual form of the vibrational mode, determined by the masses of the atoms and the electronic structure of the linkage, is essentially independent of the nature of the rest of the molecule.

The intensity of an infrared band, as well as its frequency, is determined by the electronic structure and nuclear masses of the grouping, and it follows that we may reasonably expect a characteristic group frequency to have a characteristic intensity. It should be borne in mind, however, that the measure of intensity under consideration is the absolute or integrated intensity A defined by:

$$A = \int_{\text{band}} \alpha_\nu d\nu. \tag{2}$$

The assumption that the peak extinction coefficients are also characteristic involves the additional condition that the band shapes are similar. There are apparently many exceptions to this last condition.

EXPERIMENTAL

The spectrograms shown in Figure 2 were obtained using a Baird Associates Inc. Model A infrared recording spectrophotometer (NaCl prism). The polymers were examined as thin films of unknown thickness cast on polished rock salt plates. All other spectra reported in this paper were obtained using a Perkin-Elmer Model 12A infrared spectrometer equipped with a rock-salt prism. Carbon disulfide solutions of known concentrations were used in various liquid cells of known thickness (thickness determined from interference fringes in the infrared). The slit schedule used was established to give more than adequate freedom from drift and amplifier instability and led to a half intensity slit width of between 4 and 5 cm.$^{-1}$ in the region from 680 to 1000 cm.$^{-1}$. A lithium fluoride shutter was used, and all transmission measurements were corrected for residual stray light ($\sim$1 per cent).

The naturally occurring polymers were purified by acetone extraction to remove resins and other contaminants, followed by solution in benzene and precipitation in methanol. The polyisoprene obtained from chicle was separated into *cis* and *trans* fractions by selective precipitation of the *trans* isomer from a benzene-hexane mixture at 0° C. The synthetic materials were dissolved in benzene and precipitated in methanol to remove antioxidants and other additives. All polymers were dried by the frozen benzene-sublimation method and stored in a refrigerator to prevent oxidative degradation and gelation. In the case of those polymers which were partially gelled at the time the spectra were taken, only the CS_2 soluble portion was examined.

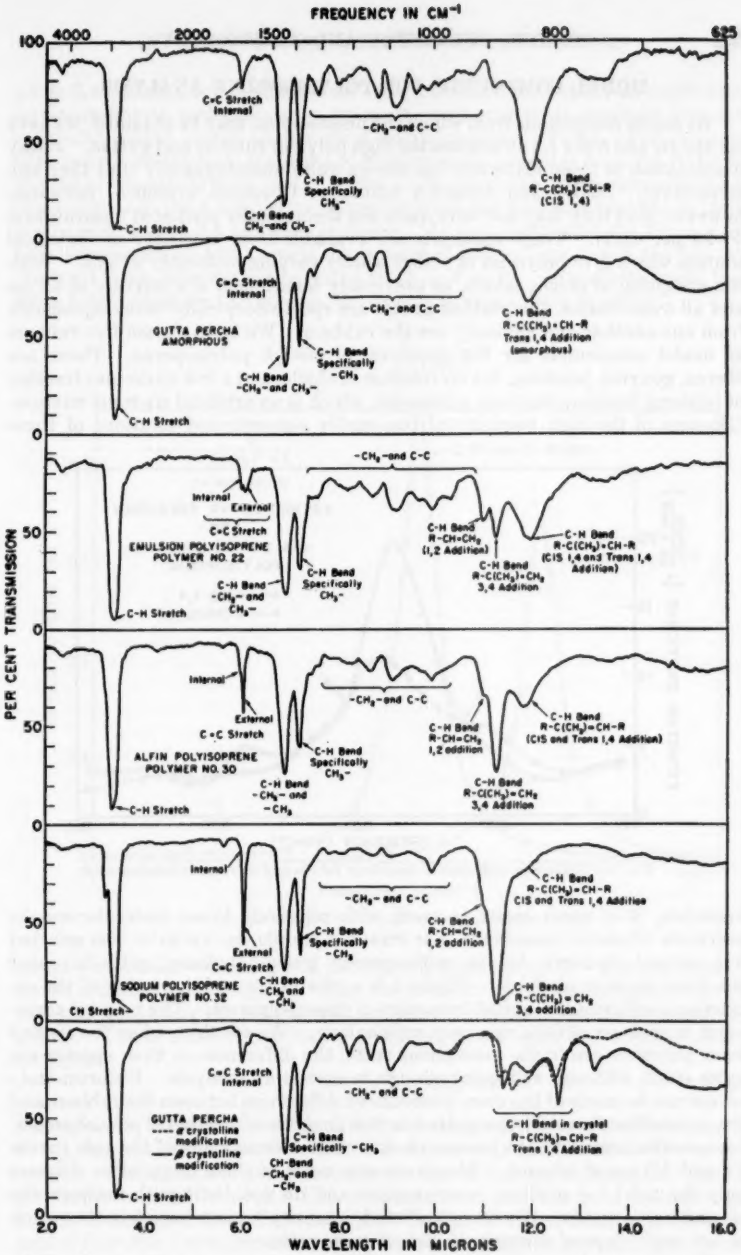

FIG. 2.—Infrared spectra of various polyisoprenes.

MODEL COMPOUNDS FOR POLYISOPRENE ANALYSIS

As model compounds from which the necessary α_{ri} may be obtained, we have for the *cis* and *trans* 1,4 structures the high polymer rubbers and guttas. *x*-Ray examination of these materials[3] has shown quite unambiguously that they are, respectively, *cis*-1,4 and *trans*-1,4 adducts. Chemical evidence[7] indicates, however, that they may not have quite the theoretically predicted unsaturation (~96 per cent). These materials are available from a variety of biological sources which give polymers of rather widely varying molecular weight. With the exception of chicle, which, as previously mentioned, is a mixture of all *cis* and all *trans* chains, the purified guttas are spectroscopically indistinguishable from one another and similarly are the rubbers. We have chosen five rubbers as model compounds for the spectrum of *cis*-1,4 polyisoprene. These are Hevea, guayule, jelutong, the *cis* fraction of chicle, and a low molecular fraction of jelutong fractionated from gutta-siak, which is an artificial *cis-trans* mixture. (Because of the high viscosity of reasonably concentrated solutions of these

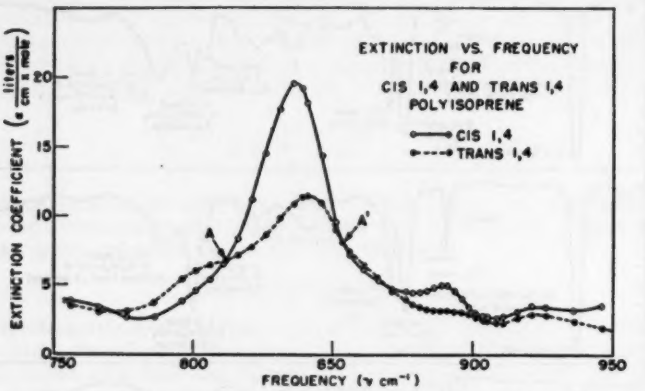

FIG. 3.—Extinction coefficient *vs.* frequency for *cis*- and *trans*-1,4 polyisoprene.

materials, it is much easier to work with relatively lower molecular-weight polymers whenever possible.) For *trans*-1,4 standards, we have also selected five natural products; balata, gutta-percha, gutta-hangkang, gutta-kay, and the *trans* fraction of chicle. Figure 3 is a plot of the average value of the extinction coefficient (α) against frequency of these polymers. The internal agreement in each set of data was very satisfactory. We see that, when the *cis* and *trans* polymers are in the amorphous state, the differences in their spectra are quite small, although still great enough to permit an analysis. Unfortunately no use can be made of the more pronounced differences between the rubbers and the crystalline forms of the guttas in the analysis of synthetic polyisoprenes, because the latter are always amorphous. The intersections of the two curves (A and A') are of interest. Measurements made at these frequencies measure only the total 1,4 addition concentration and do not distinguish between the *cis* and *trans* isomers. On the other hand, intensity measurements in the region of 840 cm.$^{-1}$ depend strongly on the *cis-trans* ratio.

There are no known high polymers of isoprene composed exclusively of the

1,2 or 3,4 addition type linkage. In order to obtain the extinction coefficients corresponding to such structures, we must carry over those obtained from low molecular-weight olefins having vinyl and isopropenyl groups. For this purpose various olefins from the series of hydrocarbons available from the National Bureau of Standards were used. Of the available olefins, three were selected as being similar to the 1,2 structure of polyisoprene and five were selected as being comparable to the 3,4 addition grouping. It was found that the three vinyl type compounds all had a single sharp band at 909 ± 1 cm.$^{-1}$ and the five isopropenyl types have similar bands at 887.5 ± 3 cm.$^{-1}$. It was also found that these bands could be fit very exactly by the inverse square function:

$$d = \frac{a}{(\nu - \nu_0)^2 + b} \tag{3}$$

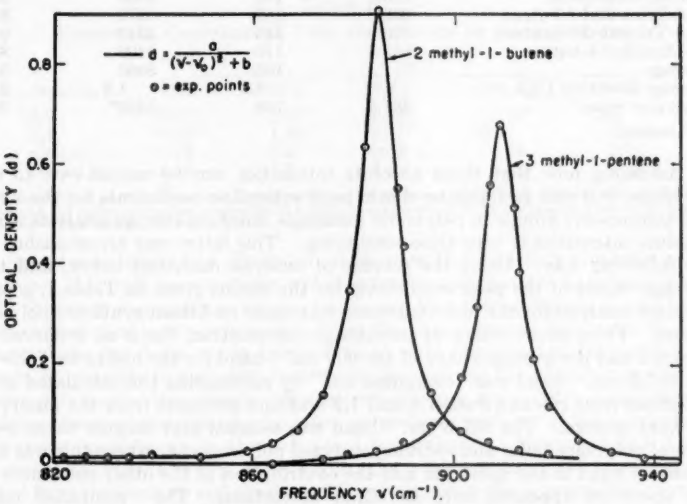

FIG. 4.—Band shapes for two low molecular-weight olefins.

where a and b are constants and the band is centered at ν_0. The exactness of the fit is illustrated in Figure 4, where the bands of two of the olefins are shown, the solid lines being the best obtainable fit of Equation (3) to the experimental points. The absolute intensities of these bands can then be evaluated analytically as:

$$A = \pi d_{\max.} \Delta\nu_{\frac{1}{2}}/2cl \tag{4}$$

where $d_{\max.}$ is the optical density at the peak and $\Delta\nu_{\frac{1}{2}}$ is the width of the band at $d = \frac{1}{2}\, d_{\max.}$. This half intensity width is related to the constant b by $\Delta\nu_{\frac{1}{2}} = \sqrt{4b}$. The results of measurements on the olefins are collected in Table I, where the half width ($\Delta\nu_{\frac{1}{2}}$) is that obtained from the best fit of Equation (3) and A is evaluated from Equation (4). It may be noted that, as is to be expected from the above discussion, the absolute intensity is more nearly constant in each series than is the peak extinction coefficient.

TABLE I

INTENSITIES OF OLEFIN BANDS

Compound	$\nu_{max.}$, cm.$^{-1}$	$\alpha_{max.}$, l. cm.$^{-1}$ mole^{-1}	A, l. cm.$^{-2}$ mole^{-1}	$\Delta\nu_{\frac{1}{2}}$, cm.$^{-1}$
		1,2 Addition Types		
1-Heptene	908.5	117	4620	10.9
1-Pentene	909.5	112	4700	11.6
3-Methyl-1-pentene	909.0	141	4590	9.04
Average		122	4580	10.5
Average deviation (%)		9.8	1.0	7.5
"Polymer value"	909.0	149	4580*	8.55
		3,4 Addition Types		
2-Methyl-2-butene	884.5	169	5630	9.20
2-Methyl-1-pentene	886.5	148	5400	9.58
2,3,3-Trimethyl-1-butene	890.0	169	5270	8.66
2,4,4-Trimethyl-1-pentene	890.0	169	5510	9.04
2,3-Dimethyl-1-butene	887.5	176	5490	8.61
Average		166	5460	9.01
Average deviation (%)		4.2	1.8	3.3
"Polymer value"	887.5	159	5460*	9.48

* Assumed.

Assuming now that these absolute intensities can be carried over to the polymers, it is still desirable to obtain peak extinction coefficients for the vinyl and isopropenyl groups in polymeric materials, since making an analysis using absolute intensities is very time-consuming. This latter was accomplished in the following way. Using the scheme of analysis described below, and the average values of the peak coefficients for the olefins given in Table I, a preliminary analysis for the four structures was made on fifteen synthetic polyisoprenes. From these values of percentage composition, the α *vs.* ν curves in Figure 3 and the average shape of the 909 cm.$^{-1}$ band for the olefins in Table I, the 887.5 cm.$^{-1}$ band was "computed out" by subtracting the calculated contributions from *cis*- and *trans*-1,4 and 1,2 addition products from the observed polymer spectra. The 887.5 cm.$^{-1}$ band was selected first because there were several polymers (alfin and sodium catalyzed polyisoprene) where this was the strongest band in the spectrum and the contribution of the other structures to the spectrum appeared only as minor corrections. The "computed out" 887.5 cm.$^{-1}$ bands for the polymers were then fitted with Equation (3) and, from the value of b obtained from the best fit, $\Delta\nu_{\frac{1}{2}}$ was calculated. Finally, from the accepted value of A in Table I and this value of $\Delta\nu_{\frac{1}{2}}$, the value of $\alpha_{max.}$ for the polymer was obtained from Equation (4). Once this new shape of the 887.5 cm.$^{-1}$ band was established, a similar procedure was carried out for the 909 cm.$^{-1}$ band; and, finally, the whole iterative procedure was repeated without achieving further refinement. These new "polymer values" of $\alpha_{max.}$ at 887.5 cm.$^{-1}$ and 909 cm.$^{-1}$ are also given in Table I. In the course of these refinements it was also found necessary to shift the α *vs.* ν curves for the *cis*- and *trans*-1,4 compounds about 4.0 cm.$^{-1}$ to higher frequency. The reason for this shift is not clear, but, unless it was used, the agreement between the points A and A′ for total 1,4 addition was not very satisfactory, and the calculated band shapes given below were shifted from the observed bands.

Assuming now that we know the $\alpha_{\nu i}$ as a function of frequency for the four structures arising from *cis*- and *trans*-1,4, 1,2, 3,4 addition in the synthetic polymers, it remains only to select the four frequencies at which the analysis is to

be made. We have selected, of course, 887.5 cm.$^{-1}$ and 909 cm.$^{-1}$ where the 3,4 and 1,2 adducts are the principle absorbers respectively. For the 1,4 addition, we have used 815.5 and 857.0 cm.$^{-1}$ (points A and A′ in Figure 2 shifted 4.0 cm.$^{-1}$ to higher frequency) which depend only on the total 1,4 addition and do not differentiate between *cis* and *trans* (one of these is of course redundant and serves only as a check on the other). To establish the *cis-trans* ratio, we use 843.0 cm.$^{-1}$ midway between the maxima of the *cis* and *trans* peaks (shifted). At these frequencies we then have five equations of the type of Equation (1), and these are solved by successive approximations to give the analysis of an unknown. The two values obtained from 815.5 cm.$^{-1}$ and 857.5 cm.$^{-1}$ for the concentration of 1,4 adduct were averaged to obtain the percentages of 1,4 given below. The values of the extinction coefficients used in the final analyses are given in Table II.

TABLE II

EXTINCTION COEFFICIENTS USED IN ANALYSIS OF POLYISOPRENES

	ν, cm.$^{-1}$				
Structure	815.5	843.0	857.5	887.5	909.0
1,2	0.31*	0.62*	1.02*	5.73*	149
3,4	0.69*	1.80*	3.87*	159	7.48*
cis-1,4	6.78	19.2	8.06	4.56	2.72
trans-1,4	6.78	11.3	8.06	3.26	2.40

* These values were obtained from Equation (3) and the polymer values of $\alpha_{max.}$ and $\Delta\nu_{\frac{1}{2}}$ given in Table I. In general, the olefins showed no absorption at these frequencies which could not be accounted for as arising from the "wings" of the 887.5 or 909.0 cm.$^{-1}$ bands.

Before proceeding to a discussion of the results for various synthetic polyisoprenes, it should be noted that rather extensive assumptions have been made as to the exact shapes of the various bands and that these assumed shapes have been carried over to the polymers. From this it is apparent that, even though the analysis has been made using data at only five selected frequencies, it should be possible to calculate back from the analysis the complete spectrum of the polymer in this region. Agreement between the spectra so calculated and the observed spectra may be taken as evidence in favor of the correctness of our assumptions as to the individual band shapes. Figures 5 and 6 are typical of the results of such calculations; the solid lines being the spectra computed from the analysis and the dashed lines and points the experimental curves. The agreement is seen to be quite satisfactory.

To summarize: The extinction coefficients for *cis-* and *trans*-1,4 addition were obtained from naturally occurring polymers by shifting their absorption curves by 4.0 cm.$^{-1}$ to higher frequency. The peak extinction coefficients for 1,2 and 3,4 addition in polyisoprene were obtained from the average absolute intensities of low molecular-weight olefins and the average band widths in polymers, assuming that the bands have the inverse square shape given by Equation (3). It is felt that this approach is theoretically more sound than carrying over the olefin peak intensities directly.

RESULTS OF ANALYSES

Table III is a list of the various polyisoprenes which were investigated and the percentage composition found in each case. Data on the methods by which the polymers were prepared include the preparation phase and temperature, the catalyst, and the per cent conversion of monomer to polymer. For reasons noted below, the percentages of the adducts reported are normalized to the

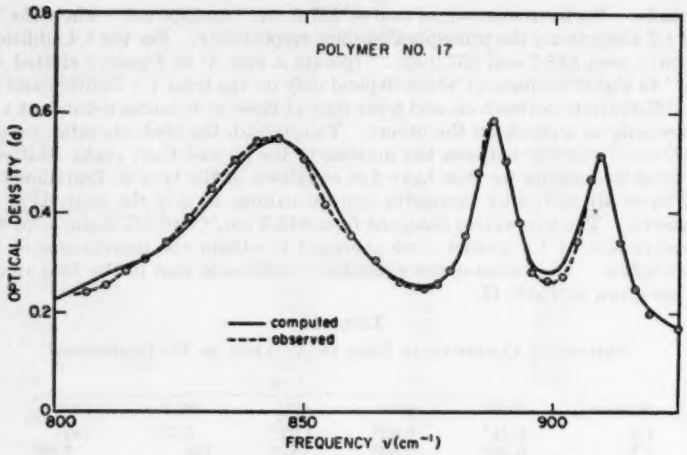

FIG. 5.—Computed and observed spectrum of Polymer No. 17 (emulsion polyisoprene).

total found concentration in each case and not the made-up concentrations. The column titled "% found" is the ratio of the found concentration to the made-up concentration expressed as per cent.

ERRORS

Several sources of possible errors in these measurements should be mentioned. Two properties of the polymers themselves combine to cause most of

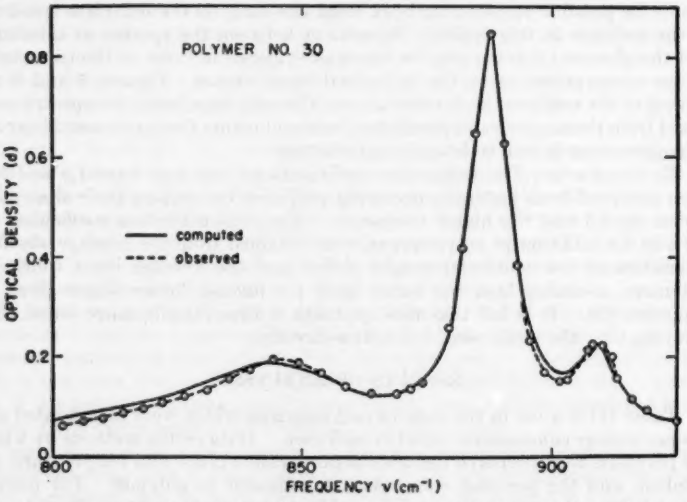

FIG. 6.—Computed and observed spectrum of Polymer No. 30 (alfin polyisoprene).

TABLE III

EXPERIMENTAL RESULTS

Polymer No.	Preparation phase	Preparation temp. (° C)	% conversion	Catalyst	% 1,2	% 3,4	% 1,4	% *cis*	% *trans*	% found	Source
1*	Emulsion	−20	50	Polyamine†	5.3	4.5	90.2	0	90.2	113	a
2	Emulsion	−20	50	Polyamine	4.9	4.5	90.6	3.1	87.5	116	a
3*	Emulsion	−17.8	21	Polyamine	5.1	4.0	90.9	0	90.9	103	b
4*	Emulsion	−17.8	39	Polyamine	5.6	5.0	89.4	10.2	79.2	96.2	b
5*	Emulsion	−17.8	59	Polyamine	5.5	5.0	89.5	7.6	81.9	99.5	b
6	Emulsion	−5	25	Polyamine	5.5	5.1	89.4	6.1	83.3	105	a
7	Emulsion	−5	55	Polyamine	5.2	4.6	90.2	5.7	84.5	139(?)	a
8	Emulsion	5	~5	Cumene hydroperoxide	5.9	5.3	88.8	9.7	79.1	105	a
9	Emulsion	5	58	Cumene hydroperoxide	6.7	5.4	87.9	1.7	86.2	108	c
10	Emulsion	10	22	Polyamine	5.6	5.2	89.2	11.9	77.3	103	b
11	Emulsion	10	40	Polyamine	5.3	5.0	89.7	11.2	78.5	102	b
12	Emulsion	10	59	Polyamine	5.5	5.0	89.5	10.8	78.7	103	b
13	Emulsion	25	30	Light	5.1	5.1	89.8	8.5	81.3	109	a
14	Emulsion	43.9	21	Light	4.7	5.0	90.3	13.6	76.7	107	b
15	Emulsion	43.9	42	Light	5.0	5.1	89.9	6.3	83.6	111	b
16	Emulsion	43.9	60	Light	5.0	5.1	89.9	13.1	76.8	110	b
17	Emulsion	50	13	Potassium persulfate	5.4	5.4	89.2	12.5	76.7	104	a
18	Emulsion	50	22	Potassium persulfate	4.7	5.1	90.2	6.4	83.8	116	b
19	Emulsion	50	41	Potassium persulfate	5.9	6.2	87.9	29.2	58.7	88.9(?)	b
20	Emulsion	50	50	Potassium persulfate	5.2	5.3	89.5	17.6	71.9	106	a
21*	Emulsion	50	55	Potassium persulfate	5.4	4.9	89.7	18.9	70.8	98.4	b

TABLE III—(*Continued*)

Polymer No.	Preparation phase	Preparation temp. (° C)	% conversion	Catalyst	% 1,2	% 3,4	% 1,4	% *cis*	% *trans*	% found	Source
22	Emulsion	55	58	Potassium persulfate	5.3	6.6	88.1	10.1	78.0	107	a
23	Bulk	20	5	Oxygen	5.1	5.0	89.9	4.1	85.8	110	a
24	Bulk	70	15.6	Diazoaminobenzene	5.4	5.9	88.7	28.8	59.9	98.3	a
25	Bulk	70	22	Cumene hydroperoxide	5.5	6.0	88.5	25.3	63.2	98.8	a
26	Bulk	70	26	Lauryl peroxide	5.1	5.8	89.1	22.7	66.4	96.6	a
27	Bulk	70	55	Cumene hydroperoxide	5.4	6.5	88.1	22.5	65.6	93.8	a
28	Bulk	120	35	Cumene hydroperoxide	5.2	6.0	88.8	23.3	65.5	100	a
29	Solution	25	34	Alfin‡	4.6	22.5	72.9	2.3	70.6	114	d
30	Solution	40	19	Alfin	5.0	24.2	70.8	10.9	59.9	98.8	d
31	Solution	40	52.9	Alfin	4.5	22.3	73.2	0.7	72.5	107	d
32	Solution	30	50	Sodium	6.6	55.0	38.4	0	38.4	107	e
33	Solution	50	90	Sodium	5.2	43.3	51.5	0	51.5	104	e
34	Solution	20	~10	Boron trifluoride	3.4	6.1	90.5	0	90.5	74.0	a
35	Solution	20	~10	Boron trifluoride	4.0	7.1	88.9	0	88.9	51.2	a
36	Chicle				0	0	100.0	35.0	65.0	102	

* Low intensity spectrum; see section on *ERRORS*. † Polyamine plus a hydroperoxide of the cumene type. ‡ Sodium isoproperoxide and allyl sodium.
(a) This laboratory.
(b) J. D. D'Ianni, The Goodyear Tire & Rubber Company.
(c) U. S. Government Laboratories, University of Akron.
(d) A. A. Morton, Massachusetts Institute of Technology.
(e) C. S. Marvel, University of Illinois.

the experimental difficulty. First, the *cis*-1,4 and *trans*-1,4 structures which are generally predominant, are not very strong absorbers. This means that one must go either to fairly concentrated solutions or to long path lengths to obtain absorptions which are great enough to measure accurately. Second, because of the high molecular weight of these materials, their solutions tend to be very viscous. The possibility of using dilute solutions in thick cells is, of course, limited by the transparency of the solvent used. In the case of carbon disulfide, which is probably the best solvent for this spectral region, serious difficulty from solvent absorption is encountered in the region of 860 cm.$^{-1}$ at thickness much greater than 0.5 mm. A single cell of thickness 0.528 mm. was used in almost all of the measurements reported here. With this thickness, solutions of the order of 5 g. per 100 ml. were generally required to give reasonable absorptions, and this often led to solutions having the consistency of a very thick glue. The difficulties of getting such solutions into thin infrared cells without loss of the very volatile solvent are obvious. It is felt that this difficulty is the main cause of the trend towards finding a higher concentration of components than the made-up concentration.

Provided the product cl is great enough to give optical densities of about 0.3 to 0.6 in the regions of interest, the spectrographic errors are probably not more than 1–2 per cent. However, in some cases it was necessary to dilute the polymer solutions to the point where peak optical densities were only ~0.2. In these cases (marked with an asterisk after the polymer number in Table III) the errors in the spectrographic measurements may be somewhat more serious.

The tendency of the analyses to show more than 100 per cent of the made-up concentration perhaps merits further attention. As mentioned above, the most likely source of this difficulty is loss of solvent during the slow process of filling the cell. Some other explanations of this deviation are also possible, however. First, there is indication in the literature[7] that the synthetic polyisoprenes do have higher unsaturation (~98–100 per cent of theoretical) than the natural product polymers (~96 per cent of theoretical) from which the a_{ri}'s were obtained. Second, there exist in the synthetic polymers fragments of catalyst molecules which, although present in low concentration in the polymer, may have some absorption in the region used in the analyses. The combination of these possible reasons for finding more than 100 per cent of the made-up concentration leads us to report the analyses normalized to the found concentration rather than to the made-up concentration.

Special mention should also be made of the possible magnitude of errors in the determination of the *cis/trans* ratio. Because the extinction of *cis*-1,4 and *trans*-1,4 adducts differ by at most a factor of two, rather small errors in the optical density measurement at 843.0 cm.$^{-1}$ can lead to wide variation in the *cis/trans* ratio. For this reason we set the rather large limits of ±5 per cent for the per cent of *cis* and per cent of *trans* in the total polymer analysis. In the cases marked with an asterisk even larger (~10 per cent) errors may be present. In general, the per cent of 1,2 and per cent of 3,4 should be good to a few tenths per cent in the total analysis and per cent of 1,4 to about ±2 per cent. It may be noted that no attempt has been made to estimate errors arising from slit effects and cell thickness measurements on the extinction coefficients, or absolute intensities, since such errors tend to cancel out in the analyses.

DISCUSSION

For purposes of discussion the polymers listed in Table III can be divided into two groups: first, the bulk and emulsion polymers prepared with free

radical catalysts (Nos. 1–28) and, second, the polymers prepared in solution with other types of catalysts (Nos. 29–35). Polymer No. 36 is the unfractionated polyisoprene obtained from chicle, and if no *cis/trans* fractionation occurs on dissolving in benzene and reprecipitating in methanol, we may say the elastomer from chicle is about 35 per cent *cis*-1,4 and 65 per cent *trans*-1,4.

FREE RADICAL CATALYZED POLYMERS (NOS. 1–28)

Bearing in mind the limits of error set for these results, we may say that, for the free radical initiated polymers, we find no effect of phase (bulk *vs.* emulsion), specific catalyst, or conversion on the polymer structure. Of the variables given, the only one which obviously affects the structure is the polymerization

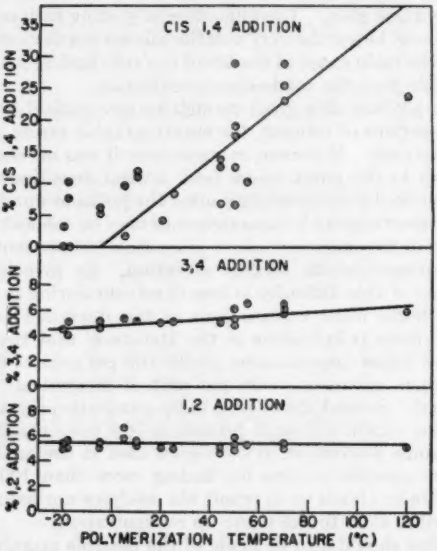

FIG. 7.—Variation of structure with polymerization temperature for free radical initiated polyisoprenes (emulsion and bulk).

temperature. The variation of the composition with preparation temperature is shown in Figure 7. The solid lines in each case are the straight lines fitted to the data by the method of least squares. In the case of the per cent *cis*-1,4 *vs.* temperature, the line probably reaches essentially zero per cent *cis* somewhere in the neighborhood of 0° C, and only the points above 0° were used to determine the least square line. The bad scattering of the points in this case is merely a reflection of the difficulty in accurately determining the *cis/trans* ratio.

As can be seen from these graphs, the amount of 1,2 addition is essentially independent of temperature at a level of about 5.5 per cent, while the amount of 3,4 addition changes from about 4.5 to about 6 per cent in the temperature range −20 to 100° C. The per cent of 1,4 adduct shows a corresponding decrease from about 90 to about 88.5 per cent over this range. The most striking

change is, of course, the increasing incidence of *cis*-1,4 as the temperature is raised; polymers prepared below 0° C having essentially no *cis*-1,4, while at 100° C the incidence is about 25 per cent.

ALFIN–CATALYZED POLYMERS (NOS. 29–31)

The polymers prepared with alfin catalysts, when compared to free radical initiated polymers, show an increased amount of 3,4 addition at the expense of 1,4 adduct; the level of the 1,2 adduct being essentially the same as in the case of the free radical catalyzed polymers. Little significance is attached to the values of per cent of *cis* and per cent of *trans* in these materials because the level of 1,4 absorption was too low to obtain an accurate *cis/trans* ratio.

SODIUM CATALYZED POLYMERS (NOS. 32 AND 33)

These materials show an even greater amount of 3,4 addition than the alfin polymers; and again, this is at the expense of 1,4 addition with the 1,2 addition remaining at the 5 per cent level as in free radical polymers. Here also no significance can be attached to the *cis/trans* ratio.

CATIONIC CATALYZED POLYMERS (NOS. 34 AND 35)

The two polymers prepared with BF_3 are of interest since the total found concentration of double bonds is much less than 100 per cent. While explanations have been advanced for the general tendency of the analyses to total more than 100 per cent, finding less than 100 per cent can only mean a loss of double bonds during polymerization. It is well known that BF_3 is a catalyst for the isomerization (cyclization) of rubber, and the results of the analyses indicate that some reaction leading to the loss of the normally stable double bonds of polyisoprene occurs during the course of the polymerization. The linear polyisoprene which is present to about 50 per cent in Polymer No. 35 and about 75 per cent in Polymer No. 34 appears to have about the same distribution of 1,2, 3,4, and 1,4 addition as the free radical initiated polymers.

COMPARISON OF RESULTS WITH OTHER DATA

The results of this analysis are in good agreement with the results of the perbenzoic acid reaction for the ratio of external to internal double bonds[7].

In the isoprene polymers, 3,4 addition (as defined in Figure 1) is analogous to 1,2 addition in the polybutadienes. The results given here for polyisoprenes are rather similar to analyses obtained by other workers[8] on the polybutadiene system. In the polyisoprenes, compared to the polybutadienes, the incidence of external double bonds is somewhat lower in all types of polymers. However, the temperature dependence of the concentration of external double bonds is essentially the same. Similarly the incidence of *cis*-1,4 addition and its change with polymerization temperature is essentially identical with the case of the butadiene polymers.

SYNOPSIS

The infrared spectra of synthetic polyisoprenes have been used to obtain quantitative analyses for the various types of addition occurring in the polymers. It is found that the composition of polymers prepared in bulk and emulsion systems is, within experimental error, independent of specific catalyst

and per cent conversion of monomer to polymer. The structure of these materials is affected by preparation temperature, increasing temperature leading to a slight increase in 3,4 addition and a large increase in *cis*-1,4 addition. Polymers prepared in solution with alfin and sodium catalysts show increased amounts of 3,4 addition at the expense of 1,4 addition. Polymers prepared with a cationic catalyst (BF_3) are apparently not exclusively linear polyisoprenes.

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REFERENCES

[1] Field, Woodford, and Gehman, *J. Applied Physics* **17**, 386 (1946); D'Ianni, *Ind. Eng. Chem.* **40**, 253 (1949).
[2] Gehman, *Chem. Revs.* **26**, 203 (1940).
[3] Schlesinger and Leeper, *Science* **112**, 51 (1950).
[4] Field, Woodford, and Gehman, *J. Applied Physics* **17**, 386 (1946).
[5] Dinsmore and Smith, *Anal. Chem.* **20**, 11 (1949).
[6] Saunders and Smith, *J. Applied Physics* **20**, 953 (1949).
[7] D'Ianni, *Ind. Eng. Chem.* **40**, 253 (1949).
[8] Hampton, *Anal. Chem.* **21**, 923 (1949); Hart and Meyer, *J. Am. Chem. Soc.* **71**, 1980 (1949).

INVESTIGATION OF THE ROLE OF INTERMOLECULAR FORCES IN THE MECHANISM OF HIGH-ELASTIC DEFORMATION. VII. THE EFFECT OF MOLECULAR INTERACTION ON THE FATIGUE RESISTANCE OF HIGH POLYMERS HAVING HIGHLY DEVELOPED SPATIAL STRUCTURES *

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In a previous article[1] it was shown that a decrease of the potential energy of the molecular reaction of vulcanizates is accompanied by an increase of their fatigue resistance up to a certain limit, beyond which a further decrease of the molecular reaction leads to a lowering of the fatigue resistance of the vulcanizates. The non-uniform change of fatigue resistance was explained by the fact that, with a decrease of the molecular reaction, the mechanical losses, a part of which go into the activation of the chemical processes leading to destruction of the rubber, are also lowered. However, parallel to the decrease of the molecular reaction, a decrease of the tensile strength is observed. The superposition of the decrease of mechanical losses during deformation and the decrease of tensile strength which are observed simultaneously during decrease of the molecular reaction leads to a non-uniform change of fatigue resistance. The method of swelling vulcanizates in paraffin oil and dibutyl phthalate was used in measuring the potential energy of intermolecular reaction. It was interesting to study the behavior of loaded as well as unloaded vulcanizates of natural rubber, and also to study rubbers with various concentrations of molecularly reactive groups.

In this article, experimental data are presented which confirm the concepts stated above and furnish a more detailed analysis of the phenomena which are associated with the fatigue of vulcanizates.

In comparing the fatigue resistance of various vulcanizates, the question arises as to the correct method for making such a comparison; i.e., whether to test the vulcanizates at a constant deformation, or to maintain a constant deforming load. It was desirable to test the fatigue resistance of specimens in such a way that, with a decrease of molecular reaction, the work of deformation would not decrease, for in such a case the increase of fatigue resistance might be attributed to this effect.

The application of the equation proposed by Flory, as was done in the earlier work[1], is not sufficiently convincing, since the results of the calculations in this case depend on whether the deforming force is applied to the swollen or to the non-swollen specimen. An approximate but therefore more graphic method involves the assumption of Hook's law as valid in the conditions of

* Translated for Rubber Chemistry & Technology from the *Kolloidnyi Zhurnal*, Vol. 15, No. 1, pages 1–10 (1953).

deformation. Then, with constant deformation for all vulcanizates, we have:

$$W = \int_{\epsilon_1}^{\epsilon_2} \sigma d\epsilon = \int_{\epsilon_1}^{\epsilon_2} E\epsilon d\epsilon = \left| \frac{E\epsilon^2}{2} \right|_{\epsilon_1}^{\epsilon_2} \quad (1)$$

where ϵ_1 and ϵ_2 are the minimal and maximal relative elongations of the specimen, in the process of repeated deformation; E is the modulus of elasticity, and σ is the stress.

The relation obtained attests to the fact that, in any comparison of specimens with different moduli of elasticity or at identical deformations, the specific work of deformation expended is smaller, the smaller is the modulus of elasticity.

The inverse relation holds true when specimens are tested under constant stress:

$$W = \int_{\sigma_1}^{\sigma_2} \sigma d\epsilon = \int_{\sigma_1}^{\sigma_2} \frac{\sigma d\sigma}{E} = \left| \frac{\sigma^2}{2E} \right|_{\sigma_1}^{\sigma_2} \quad (2)$$

Thus, in order to confirm experimentally the increase of the creep of vulcanizates at the expsense of a decrease of energy loss during deformation, it was necessary to make tests with a uniform deforming load, maintaining constant the geometric dimensions of the specimens.

To determine the degree of heat build-up and the mechanical losses at various degrees of swelling, vulcanizates of natural rubber containing 30 per cent carbon black were prepared. The heat build-up was measured on a Goodrich apparatus at a frequency of deformation of 1040 cycles per minute. The temperature was measured inside the specimen and on its surface (which increases with the time of fatigue).

The temperature change of a swollen specimen as a function of the time of testing is shown in Figure 1, from which it is seen that, with reported deformations, the temperature of the specimen at first increases sharply, reaching a certain value A', after which the change of temperature with time of fatigue becomes smaller and shows a linear relation. The nature of the curve indicates that, as it approaches the point A, equilibrium is established between the heat liberated in the process of repeated deformation and the heat dissipated into the surrounding medium. In the beginning, when the amount of heat liberated is much greater than the amount of heat dispersed into the surrounding space, the temperature within, as well as on the surface of the test-specimen, increases rapidly. The rate of increase of the temperature becomes smaller as the temperature approaches the value A'. Starting at a temperature equal to A', the rate of temperature increase becomes almost constant, which reveals the course (at the same time as the increase of temperature because of mechanical losses) of the process of heat formation because of chemical changes. If there were no chemical changes in the fatigue process, a constant temperature would then be established at the time A. This constant temperature value can be estimated by extrapolating a rectilinear segment of the curve to its intersection with the temperature axis, as shown in Figure 1. The value K obtained is the temperature which would be established as a result of the equilibrium between the heat liberated in the fatigue process and that dissipated into the surrounding space, i.e., the inclination of the rectilinear segment of the curve tan φ, indicates the intensity of the chemical processes in the vulcanizate. During repeated deformations, the mechanical loss for each deformation cycle remains constant. More accurately, the loss decreases somewhat as a result of the decrease of internal friction with increase of temperature of the specimen.

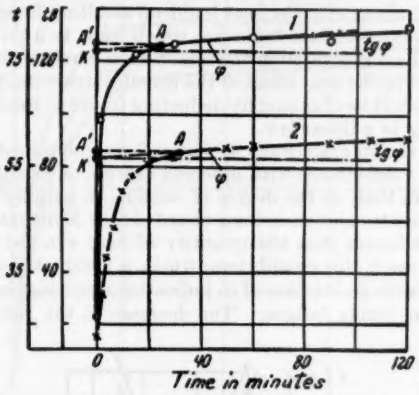

FIG. 1.—Relation of temperature of test-specimen to time of repeated deformation.
1. Internal (t_s). 2. Surface (t).

If different amounts of heat are generated in a unit of time, the rubber will gradually become hotter until the amount of heat formed in a unit of time equals the amount of heat evolved into the surrounding space. If the amount of heat entering the test-specimen in a unit of time is greater, then the equilibrium temperature and the rate at which it is reached change correspondingly. The nature of the $t^0 - t$ curve must remain constant.

In case an equilibrium temperature is not established, there must be an increase of the amount of heat generated. This increase of heat can not be attributed to the increase of mechanical losses due to the causes explained above.

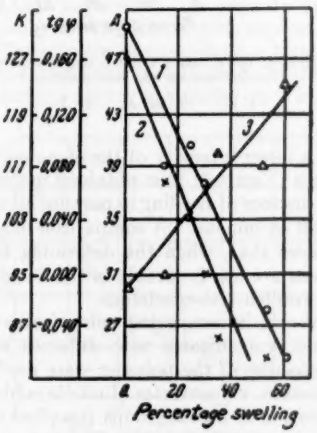

FIG. 2.—Relation of K, tan φ, and A to the degree of swelling in paraffin oil (the deforming load was kept uniform).
1. K. 2. tan φ. 3. A.

Consequently, along with the heat build-up resulting from internal friction, there is another source of heat build-up, which leads to a progressive increase of the amount of heat generated in the specimen in a unit of time. This source of heat is manifest in the heat effect of the chemical reactions; thus the equilibrium temperature will be obtained by deducting from the total temperature the increase according to a linear law.

The relations shown graphically in Figure 2 were obtained from a comparison of curves for vulcanizates with different degrees of swelling in paraffin oil.

Figure 2 shows that, as the degree of swelling in paraffin oil increases, the equilibrium temperature between the amount of heat K liberated and dissipated decreases; this indicates that the quantity of heat evolved is smaller. The time required to reach this equilibrium, which is designated in Figure 2 by A, increases greatly with an increase of Q, indicating a slowing down of the process of heat formation during fatigue. The decrease of the values of tan ϕ with

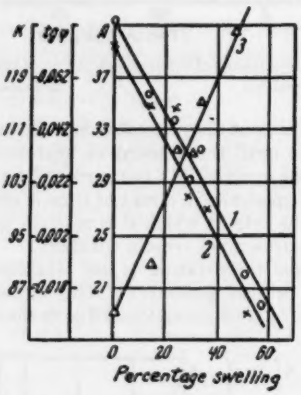

FIG. 3.—Relation of K, tan φ, and A to the degree of swelling in paraffin oil (the deformation was kept uniform).

1. K. 2. tan φ. 3. A.

increase of Q indicates a lesser intensity of the chemical processes. Analogous relations for K and tan ϕ (Figure 3) were obtained in the case of fatigue of vulcanizates with various degrees of swelling in paraffin oil under conditions of constant deformation for all specimens. A comparison of the slopes of the curves of Figures 2 and 3 shows that, when the deforming load is constant for all specimens, the conditions are less favorable to the development of heat formation in the case of the swollen test-specimens.

As already stated above, in comparing vulcanizates having different intermolecular energy values, vulcanizates with different contents of polar atom groups in the chain molecules of the polymer were used. In order to exclude the influence of other factors, vulcanizates of nitrile rubbers were chosen, which differed in the concentration of nitrile groups (smallest concentration in No. 1, largest in No. 3), but with equally developed spatial structure[2].

Figure 4 shows the time-temperature curves for vulcanizates of rubbers Nos. 1, 2, and 3.

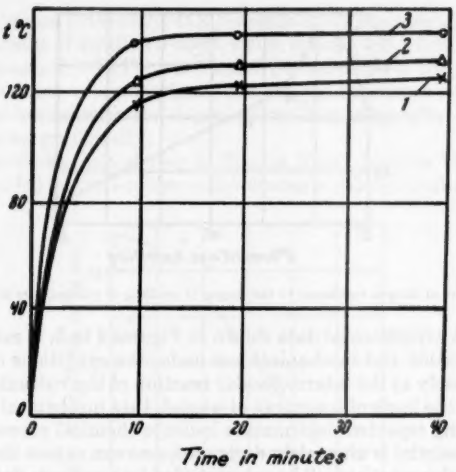

FIG. 4.—Relation of temperature inside a test-specimen to the time of repeated deformation.

1. Vulcanizates of No. 1 rubber.
2. Vulcanizates of No. 2 rubber.
3. Vulcanizates of No. 3 rubber.

On the basis of the data shown in Figure 4, it may be concluded that the increase of concentration of the polar groups and, consequently, of intensity of the intermolecular action, is accompanied by an increase of heat formation in the process of repeated deformation; this accords well with the reasoning above.

Measurement of the temperature of specimens during repeated deformation makes it possible to judge only the mechanical losses which result in the increase of the kinetic energy of heat movement. In order to obtain a more complete idea of the mechanical losses in vulcanizates with various values of intermolecular energy, the phase difference was measured on a Kornfeld machine.

The change of the loss coefficient as a function of the degree of swelling of loaded vulcanizates of natural rubber in paraffin oil is shown in Figure 5. On

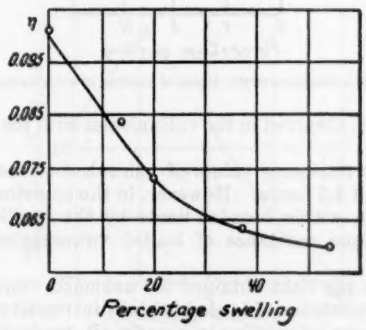

FIG. 5.—Change of coefficient of mechanical losses in relation to change of degree of swelling of vulcanizates in paraffin oil.

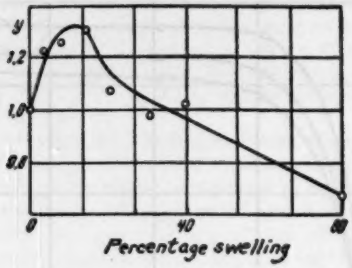

FIG. 6.—Relation of fatigue resistance to the degree of swelling of vulcanizates in paraffin oil.

the basis of the experimental data shown in Figures 2 to 5, it may be concluded that heat formation and mechanical loss under the conditions described above decrease uniformly as the intermolecular reaction of the vulcanizates decreases. Admitting, on the basis of a number of works[3], that mechanical losses and heat formation during repeated deformation indicate chemical processes, as a result of which the material is ultimately destroyed, one can expect that a decrease of the intermolecular reaction will be accompanied by a uniform decrease of fatigue resistance. In the comparison of the fatigue resistance of vulcanizates of nitrile rubbers with different concentrations of nitrile groups, the lowest fatigue

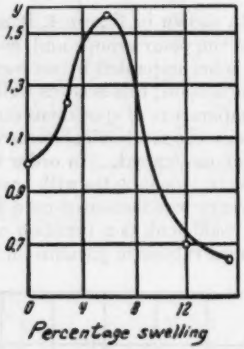

FIG. 7.—Relation of fatigue resistance to the degree of swelling of vulcanizates in dibutyl phthalate.

resistance was, in fact, observed in the vulcanizates with the most intense intermolecular action.

Thus, the fatigue resistance values of vulcanizates Nos. 1, 2, and 3 were, respectively, 1, 2, and 4.5 hours. However, in the experiments on the change of molecular reaction within broader limits by the swelling method, it was shown that the fatigue resistance of loaded vulcanizates does not change uniformly.

Corresponding to the data obtained for unloaded vulcanizates of natural rubber[1] the fatigue resistance of loaded rubbers increased proportionally with an increase of the degree of swelling in paraffin oil, reached a maximum value, then decreased uniformly.

As has been stated previously, this decrease of fatigue resistance can explain the marked decrease of tensile strength which is observed when certain degrees of swelling are reached. In Figures 6 and 7 the variation of the relative fatigue resistance (as a basis of comparison, the fatigue resistance of an unswollen vulcanizate was taken) with the degree of swelling in paraffin oil and dibutyl phthalate is shown graphically.

Comparison of the data shown in Figures 6 and 7 shows that, during the swelling of unloaded natural-rubber vulcanizates in dibutyl phthalate, the maxi-

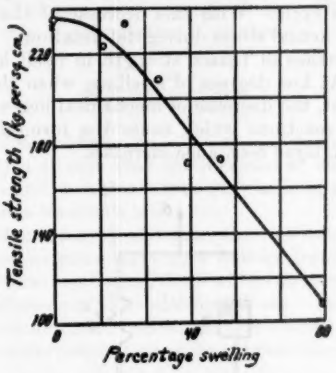

FIG. 8.—Change of tensile strength of loaded vulcanizates in relation to the degree of swelling in paraffin oil.

mum increase of fatigue resistance is much larger than in the case of swelling in paraffin oil, and this value is reached at lower degrees of swelling than with paraffin oil as solvent.

The results of measurements of the tensile strength of unloaded vulcanizates showed that the tensile strength changes in proportion to the swelling in paraffin oil, at first slightly, then, beginning with swelling of 10 per cent, the fall of tensile strength becomes much sharper (see Figure 8).

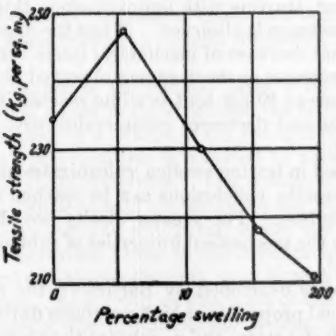

FIG. 9.—Change of tensile strength of loaded vulcanizates in relation to the degree of swelling in dibutyl phthalate.

Figure 9 shows the change of tensile strength during swelling in dibutyl phthalate. At low degrees of swelling, the tensile strength increases, again reaching the values of an unloaded vulcanizate, where Q is 10 per cent. When a vulcanizate is subjected to repeated deformation, it is weakened as a result of the development of chemical processes which lead to the accumulation of micronuclei of destruction. This weakening is caused by an increase of the number and size of these micronuclei and a change of structure and of other properties until the effective tensile strength of the specimen in the given section is so small that the specimen cannot withstand the highest stress undergone during a deformation cycle. With this decrease of the tensile strength, the latter approaches the actual stress during deformation.

Therefore the decrease of tensile strength in itself leads to a decrease of fatigue resistance. At low degrees of swelling, when the decrease of fatigue resistance is still slight, the decrease of mechanical losses prevents the intensification of chemical reactions which cause the formation of micronuclei of destruction, and the fatigue resistance increases.

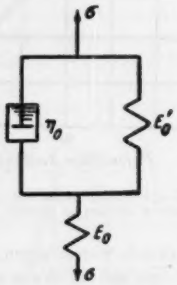

FIG. 10.—Alexandrov's model, representing the mechanical properties of vulcanizates.

During swelling of loaded vulcanizates in paraffin oil, the mechanical losses decrease particularly sharply when the degree of swelling increases from 0 to 20 per cent. But, starting from 10 per cent swelling, the tensile strength decreases sharply, so that, starting with approximately this degree of swelling, a decrease of fatigue resistance is observed. When the degree of swelling reaches 40 per cent, any further decrease of mechanical losses becomes very slight, but the tensile strength decreases as much as was observed above 10 per cent swelling. Fatigue resistance at 40 per cent swelling reaches its maximum value for unswollen vulcanizates and decreases considerably with a further increase of the degree of swelling.

The results obtained in testing swollen vulcanizates are interesting because, on the basis of such results, conclusions can be reached concerning the mechanism of fatigue of rubber. For greater clarity we shall use the modulus (Figure 10) describing the mechanical properties of rubbers which was proposed earlier by Alexandrov[4].

According to theories developed by Bartenev[5], the modulus in Figure 10 indicates the mechanical properties of high polymers during transition from the vitreous to the high elastic state, and η_0 denotes the viscosity for the process of orientation of the cross-links of a chain molecule; E'_0 is the initial high elastic

modulus; and E_0 is the elastic modulus. The mechanical losses, according to this modulus, depend on the rate of deformation. In the case $E_0 \gg E'_0$, we have:

$$\sigma = E'_0\epsilon + \eta_0 \frac{d\epsilon}{dt} \tag{3}$$

where E is the relative deformation; t is the deformation time; and σ is the stress.

In deformation at a definite rate, a part of the work will be expended in overcoming the internal friction of the viscous phase. This part of the work A will be greater as the rate of deformation is greater:

$$A = \eta_0\epsilon \frac{d\epsilon}{dt} = \eta_0\epsilon v \tag{4}$$

where v is the rate of deformation.

From Equation (4) it is seen that the mechanical losses increase with an increase of internal friction, but this is true only as long as the deformation of the viscous phase follows Newton's law.

With a corresponding lowering of temperature or increase of the rate, the deformation of the viscous phase no longer follows Newton's law but follows Hooke's law. Under these conditions, there will be no orientation of the kinetic elements under the influence of the deforming force. In accordance with the mechanism of deformation of solid bodies, the work consumed during deformation will be recovered in the restoration of the original form after the deforming weight is removed.

In the conditions where plastic deformation of the viscous phase begins to appear, a part of the work of deformation is irreversibly consumed by the orientation of the kinetic elements in conformity to their relative displacement. This part of the work of deformation, which is consumed in overcoming internal friction, will be greater the more complete is the process of regrouping of the kinetic elements during the action of the deforming load.

If the deformation conditions are such that, during application of the deforming load, the regrouping of the kinetic elements is complete, then a further decrease of the frequency of the deforming force is not accompanied by an increase of mechanical losses, but in this case further decrease of the deformation frequency causes a decrease of mechanical losses in a unit of time. Thus, the maximum mechanical losses occur at a definite frequency, and this is confirmed experimentally.

The molecular mechanism of mechanical losses is represented thus. As a result of the application of a load to the specimen, the latter is deformed. This deformation is accompanied by a change of the configuration of the component chain molecules; in high polymers this is manifest by successive local displacements of portions of the chain molecules. The number of these displacements is the sum of the local displacements necessary for the passage from the given configuration to the most probable configuration and the number of molecules which change their configuration owing to the deformation.

During displacement of a kinetic element, work is performed in opposition to the intermolecular forces. As a result of this, part of the work of deformation is consumed in overcoming the intermolecular action, and there are energy losses which are the sum of all the elemental factors of the displacement. The

number of elemental displacements which can take place during one deformation cycle is governed by the relation of the time of the elemental displacement to the time of a deformation cycle. In turn, the time of the elementary displacement of the kinetic units is characterized by the relaxation time.

The molecular picture presented above for the mechanism of energy losses during deformation provides an explanation of certain peculiarities of this phenomenon. As was mentioned above, the value of the mechanical losses does not change uniformly with change of the rate of deformation but passes through a maximum at definite values of the frequency of application of the deforming load. If the duration of a deformation cycle is less than the time necessary for a series of elementary displacements, the energy loss will increase with an increase of the time of application of the deformaing load, since here the number of elementary displacements during deformation increases. If the duration of a cycle is greater than the time necessary for a definite number of elementary displacements, the energy loss per cycle decreases with increase of duration of a deformation cycle.

This is explained by the fact that the work of overcoming forces of intermolecular action is expended partly at the expense of the energy of heat formation of the kinetic units. If a specimen is deformed infinitely slowly, the energy losses per deformation cycle will be zero. Zobov, Zhurkina and Kargin[6] showed, with albuminous gels, that the magnitude of relaxation processes during the deformation of high polymers is due to the nature of the intermolecular bonds which are overcome during deformation. An increase of the temperature or swelling of the polymers causes more frequent rupture of the molecular bonds because of the energy of heat formation. This is accompanied by a change of the relation between the relaxation time and the time of a deformation cycle. Thus a change of temperature or of the degree of swelling must, in general, cause irregular changes of the mechanical losses during repeated deformations. The irregular changes of mechanical losses with change of temperature have been observed several times[7] and have found a rational explanation on the basis of the schemes proposed; however, a molecular interpretation of the mechanism of energy losses during repeated deformation has not been offered.

During repeated deformation, energy losses are entailed by the mechanical activation of the chemical reactions and by the increase of the kinetic energy of heat movement, which also promotes more intense chemical reactions between the components of the system.

As a result of the chemical interaction of the components, which is localized at the points of the vulcanizates where the distribution of reactive components is most favorable to the reaction, there is, at the same time, structure formation and destruction of the rubber hydrocarbon at various locations. Here, as Karmin and Epstein showed, on the one hand, the heterogeneity of the material increases. On the other hand, the number of relaxations due to the destruction of the rubber molecules at points which form micronuclei increases. The excess strains which arise at the edges of the micro-cracks favor their gradual increase. The growth and increase of the number of these micro-cracks lead in the end to destruction of the specimen.

CONCLUSIONS

It is shown experimentally that an irregular change of the fatigue resistance of loaded natural-rubber vulcanizates with increase of the degree of swelling in paraffin oil and in dibutyl phthalate is caused by the superposition of two

processes: the increase of fatigue resistance, as a result of the reduction of mechanical losses, and the decrease of fatigue resistance due to the decrease of tensile strength proportional to the higher degree of swelling.

REFERENCES

[1] Gul, Dorokhina, and Dogadkin, *Kolloid. Zhur.* **13**, 339 (1951).
[2] Gul, Sidneva, and Dogadkin, *Kolloid. Zhur.* **13**, 422 (1951).
[3] Dogadkin and Gul, *Doklady Akad. Nauk.* **70**, 1017 (1950); *Koloid. Zhur.* **12**, 184 (1950); Kuzminskiĭ, Malzels, and Leshnev, *Doklady Akad. Nauk.* **21**, 319 (1950).
[4] Alexandrov and Lazurkin, *Zhur. Tech. Fiz.* **9**, 1249 (1939).
[5] Bartenev, *Kolloid. Zhur.* **12**, 408 (1950).
[6] Zubov, Zhurkina, and Kargin, *Kolloid. Zhur.* **9**, 367 (1947).
[7] Mikhailov, and Kirilina, *Zhur. Tech. Fiz.* **8**, 1723 (1935).
[8] Alexandrov and Lazurkin, *Kauchuk i Rezina*, 1939, No. 10, p. 34.

MECHANISM OF THE CRYSTALLIZATION OF HIGH POLYMERS*

G. SCHUUR

RUBBER-STICHTING, DELFT, HOLLAND

INTRODUCTION

The crystallization of higher polymers is a phenomenon which is not yet fully understood, one of the main difficulties being to explain how the spherulites arise.

An attempt will be made in this paper to draw a clearer picture of the mechanism of crystallization and thus to account for the origin of spherulites. It will then be seen how several other phenomena involved in the crystallization of natural rubber can be shown to be logically interrelated.

The current view is that a crystalline polymer consists of a continuous amorphous phase containing small crystalline regions, the crystallites. The evidence as to the size of these crystallites, however, is at present inconclusive, because only the lower limit of their size can be measured by means of x-ray examination. The reason is that, owing to the absence of reflections of a higher order, the effect of irregularities in the crystallites and of the heat motion of the molecules cannot be measured separately.

Another doubtful question is whether the small angle interference maxima are to be interpreted as a measure of mean distances between the crystallites. To do this, Wallner[1] has to resort to the assumption that the crystallites are unstable, whereas it is presumed, on the evidence of the mechanical properties of the high polymers, that a crystallite is stable and permanent.

Hoffmann[2] found 82 ± 7 per cent of crystalline material in polychlorotrifluoroethylene and Buckley, Cross, and Ray[3] found as much as 95 per cent in polymethylene. Such high percentages make it doubtful whether the crystalline phase can be discontinuous at all.

In this article any volume of material in which the molecules lie parallel is called a crystallite. The direction in which the molecules are oriented is termed the longitudinal direction of the crystallite. It is immaterial to the argument whether a crystallite consists of several crystallites, aligned in parallel separated by a small amount of amorphous material, or of a single crystallite containing large irregularities.

SPHERULITES

When a crystalline polymer is melted and then cooled to below its melting point, it is sometimes found to contain spherulites.

When a specimen in which spherulites occur is placed under the microscope between crossed nicols, dark crosses will be seen in a light field (Figure 1). As the specimen is rotated, the directions of the arms of a cross remain

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parallel to the directions of the polarizer and analyzer. The spherulites consist of a collection of crystallites, together forming a sphere; usually in this sphere the crystallites are aligned perpendicular to the radius[4]. Spherulites have been identified in virtually all crystalline polymers.

Kirchhof[5] has described the various forms in which spherulites occur in gutta-percha. Later, spherulites were also identified in natural rubber[6], polyethylene[4], polychlorotrifluoroethylene[7], polyamides[8], polyurethan[9], and polyethylene terephthalate[10]. They have also been found in rubber hydrochloride[11].

Various suggestions have been brought forward to account for the origin of spherulites. Jenckel and Wilsing[9] attempted to explain it on the supposition that the crystallites lie parallel to the radius of the spherulite, but, since the crystallites are usually oriented perpendicular to the radius, their argument falls to the ground.

Roseveare, Waller, and Wilson[12] and Price[7] followed out different assumptions in an endeavor to account for the existence of spherulites. Both presumed that the growth of the crystallites is preferentially in a longitudinal direction

FIG. 1.—Normal spherulite of gutta-percha between crossed nicols. Crystallized at 18° C. Magnified 270×.

by reason of the fact that the elementary units of the macromolecules engage on the principle of a zip fastener; but the existence of any such mechanism has never been proved. Even if this mechanism is accepted for the sake of argument, however, the reasoning of the two parties is not clear.

Finally, Keller[10], in view of certain variations observed in spherulites of polyethylene terephthalate, supposed that they consist of spirals, without describing the structure of explaining how this structure came into being.

None of these suggested explanations is coordinated with other aspects of crystallization.

THE MECHANISM OF CRYSTALLIZATION

(A) THE "AUTOÖRIENTATION" OF MACROMOLECULES DURING CRYSTALLIZATION

On fusing, an oriented crystalline material (such as a monofilament) shrinks longitudinally, sometimes by several hundred per cent, the dimensions in the other two special directions increasing correspondingly. The reverse takes place when oriented polymeric molecules crystallize, as the evidence of

experiments performed by Smith and Saylor[6] and Park[13] has shown. Strips of natural rubber which had been elongated several hundred per cent were found to lengthen still further on crystallizing. Reinhardt[14] found the same with polyvinylidene chloride, and rubber hydrochloride behaves similarly[11]. It is safe to assume that all high polymers display this same tendency in varying degrees.

For the purpose of explaining the mechanism of crystallization, a crystallite will now be defined as a small quantity of strongly oriented polymer. On melting, this crystallite will shorten considerably, when it will become a small quantity of amorphous material somewhere in the polymer, as represented by the cube in Figure 2. Let it be supposed that a nucleus develops in this cube, as the result of which the cube again crystallizes, with the molecules parallel to edge *a*, and that the cube will therefore stretch in this direction. This is called the *autoörientation* of the polymer. The elongation of the cube causes deformation of the surrounding material, which, consequently, continues to crystallize parallel to edge *a*, while considerable shrinkage takes place in directions *b* and *c*. As material from the surroundings has to be supplied, an

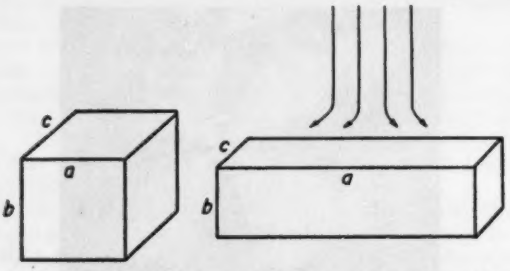

FIG. 2.—Diagram of a cube of amorphous material which stretches on crystallizing. The arrows point to amorphous material which has to be supplied from the surroundings.

orientation perpendicular to edge *a* is initiated, and as the result growth parallel to edge *a* comes to a standstill. There then remains a residual orientation at some distance, which means that nuclei are formed perpendicular to the direction of the first crystallite, for the velocity at which an oriented polymer crystallizes far exceeds that of an unoriented one. As this proceeds, the crystallites are formed parallel to the direction of stretch. Treloar[15] thoroughly investigated these phenomena with natural rubber. The new nuclei generated by the orientation will likewise grow and the process is thus repeated. In this way crystallization becomes clearly autocatalytic.

(B) THE FORMATION OF SPHERULITES

For the purpose of explaining, on the basis of the autoörientation described in the foregoing sections, how spherulites come into existence, it will be convenient to consider crystallization in a thin film, in which the crystallites lie in one plane (Figure 3).

Crystallite *A* leads to the formation of crystallite *B*, after which *C* and *D* come into existence. These crystallites can now continue to grow and, by reciprocity, will largely compensate the stresses set up by this growth. A spherulite formed in this way consists of at least four sectors which mutually

form angles of about 90°. In a given position, a spherulite of this kind is quite dark between crossed nicols; the crystallites are then parallel or perpendicular to the directions of the polarizer and analyzer. When the specimen is rotated through an angle of 45°, the spherulite becomes completely light. With a gypsum plate of red of the first order, addition is seen in two opposite sectors and subtraction in the two others. These simple "square" spherulites have actually been seen in gutta-percha on crystallization at 45° C (Figure 4). Normal spherulites are formed during crystallization at room temperature, when there is a greater tendency to crystallize and the developing structures are not so ideal. A number of crystallites will be formed at large angles until a favorable configuration has developed at the periphery, enabling the crystallites at the site to compensate each other's stresses in their further growth.

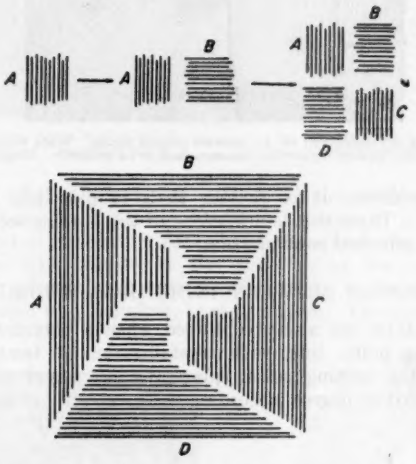

FIG. 3.—Diagram of the growth of a "square" spherulite.

This compensation may take place at a considerable distance, for the spherulites easily attain a size amounting to several tens of microns.

If films of strongly crystalline polymers, such as polychlorotrifluoroethylene, polyethylene, or gutta-percha, crystallize under the microscope between crossed nicols, the field becomes uniformly grey just before the spherulites come into existence. There is apparently very active nucleus formation in these polymers, and many randomly oriented small crystallites are formed. They can, however, only continue to grow in relative positions favorable to the mutual compensation of stresses, and it is here that the centers of the spherulites are generated. The ambient crystallites will either be destroyed or be oriented in the correct direction and absorbed in the spherulite.

When a polymer is refrigerated to below a certain temperature, the crystallites become too stable to permit the formation of spherulites, a fact which has emerged predominantly from the experimental work of Price[7]. Under these circumstances, the crystallites remain small and randomly oriented.

The above explanation also falls into line with the fact noted by Price that the growth of the radius of the spherulites is constant; in other words, crystallization is not governed by diffusion.

The essential point is the autoörientation of the molecules. All polymers exhibit this mechanism; hence all crystallizing polymers have a strong tendency

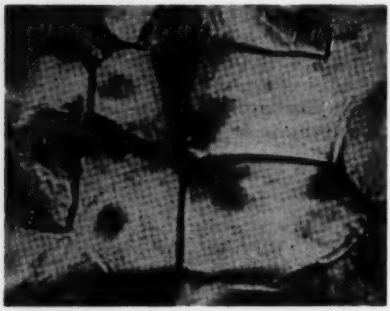

FIG. 4.—Gutta-percha, crystallized at 45° C, between crossed nicols. When the specimen is rotated through 45°, the "square" spherulite becomes dark in its entirety. Magnified 600×.

to generate spherulites. It is obvious that, in principle, the same thing happens in space. There the deformations of the various sectors compensate each other in the spherical configuration.

DIFFERENCES BETWEEN INDIVIDUAL SPHERULITES

Normal spherulites are always obtained when a polymer crystallizes far below the melting point, but, with crystallization at temperatures in the neighborhood of the melting point, spherulites are found which differ from each other in a marked degree, according to the conditions and the nature of the polymer.

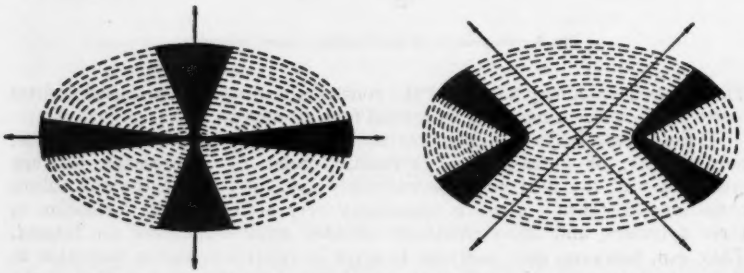

FIG. 5.—Diagram of a spherulite which is formed if there is some degree of orientation in the amorphous material. Only the cross and the hyperbolas are visible between crossed nicols. The arrows show the direction of the polarizer and analyzer.

We do not yet know enough about high polymers to be able to tell why, under certain conditions, a given type of spherulite should come into existence. We shall, however, consider some of these exceptional spherulites, when it will be seen that their formation is compatible with the general mechanism.

(1) Even after crystallization at room temperature, spherulites with a cross, the arms of which were of unequal thickness, have been seen in gutta-percha and polyethylene. When the specimen is rotated through 45°, the cross separated into two hyperbolas (Figure 5). Assuming that some orientation existed in the polymer prior to crystallization, the sectors tend to develop

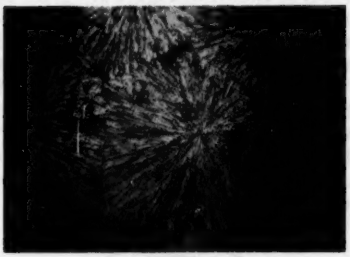

FIG. 6.—Gutta-percha, crystallized at 48° C, between crossed nicols. Magnified 100×.

FIG. 7.—Sketch of the position of the crystallites in Figure 6.

in the direction of this orientation. Thus the spherulites take on a configuration exhibiting the behavior described above. In a specimen within which some degree of orientation prevails, all the spherulites are arrayed with their longitudinal axis parallel to the direction of the orientation. The exposures of this phenomenon were too indistinct to be reproduced and a diagrammatic sketch will, therefore, have to suffice. The cross and the hyper-

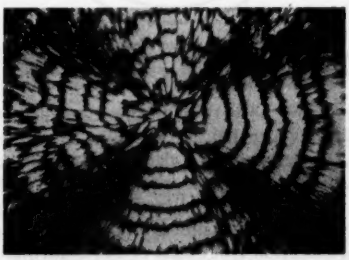

FIG. 8.—Gutta-percha, crystallized from paraffin oil at 42° C, between crossed nicols. Magnified 225×.

Fig. 9.—Sketch of the position of the crystallites in Figure 8.

bolas represented in Figure 5 are actually visualized. The direction of the orientation of the crystallites is indicated by the dotted lines.

(2) When gutta-percha crystallizes at 48° C, spherulites of dendritelike structure are formed (Figure 6). There is no axial cross and, with a gypsum plate of red of the first order, the picture presented is one of alternating small contiguous sectors with subtraction and addition. An arrangement of the crystallites in accordance with Figure 7 would account for spherulites of this kind. The crystallites reciprocally form right angles, as has been suggested.

The outward appearance is very regular and the spherulites are uniform. Hence, at low temperatures, normal spherulites are formed in gutta-percha (Figure 1), while at high temperature they are as shown in Figure 6. In the remaining range from approximately 35 to 45° C, several types of spherulites are usually found in the same specimen, as, for instance, in Figure 4.

(3) A curious picture is sometimes presented by gutta-percha, mixed with three times the quantity of paraffin oil, on crystallization at 42° C. Spherulites with certain definite layers can be observed, as shown in Figure 8. With the gypsum plate, the layers in one sector are seen to exhibit alternate subtraction and addition. The position of the crystallites in the spherulite, as suggested in Figure 9, would explain this pattern. Even without paraffin oil, definite layers have sometimes been noticed in spherulites of gutta-percha, in which, as a matter of fact, the molecules were normally oriented perpendicular to the radius. Admittedly, it was rather indistinct.

In the experiments with gutta-percha, the question as to whether it was crystallized in the α or β modification was disregarded, since this was considered to be of secondary importance in this particular investigation.

FIG. 10.—Polyethylene (alkathene 20), crystallized at 70° C, between crossed nicols. Magnified 600×.

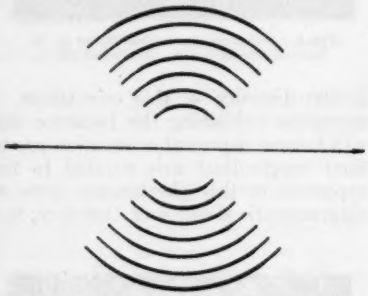

FIG. 11.—Sketch of the sectors of the rings in Figure 10 which remain visible if the light is polarized in the direction of the arrow.

(4) On crystallization at high temperature, polyethylene produces spherulites which are manifested by dark circles (Figure 10). Keller has seen these spherulites[10]. It appears, however, that the rings are also visible in unpolarized light. Under the microscope, only those sectors of the rings are seen with polarized light which are more or less parallel to the direction of vibration of the polarized light (Figure 11). As the refractive index of the crystallites only differs markedly in the longitudinal direction from that of the amorphous phase, Figure 11 becomes perfectly comprehensible if the spherulite consists of strongly crystalline layers in which the molecules are oriented in the normal way, perpendicular to the radius of the spherulite.

(5) The spherulites in polyethylene terephthalate made a particularly striking impression because the axial cross consisted of zigzag lines. At a certain temperature, Keller obtained spherulites showing a normal axial cross, but pointing in directions diverging by 45° from those of the analyzer and polarizer, with dark rings in the light sectors. This picture would be obtained if the spherulites were built up of layers of crystallites forming an angle with the radius of the spherulite. A normal axial cross, but rotated 45° relative to the directions of the analyzer and polarizer, appears if the crystallites are

arranged as shown in Figure 12. With smaller angles, the zigzag lines appear (Figure 13).

When studying these spherulites which are formed at the higher temperatures, we cannot fail to notice that usually the crystallites preferentially arrange themselves at right angles to each other. Whereas normal spherulites are formed at room temperature, when long-distance compensation of the tensions takes place we see that, at higher temperatures, crystallites which are oriented at right angles to each other are in each other's immediate vicinity. Under these circumstances, therefore, the tensions are compensated for at short distances. It is reasonable to suppose that the compensation is then more complete.

It is assumed that, far below the melting point, i.e., under definitely non-equilibrium conditions, autoörientation completely controls crystallization. That is why, under these conditions, all high polymers produce spherulites of approximately the same configuration. In the neighborhood of the melting

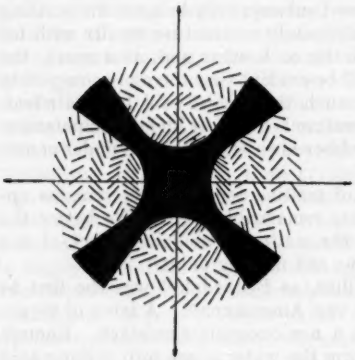

FIG. 12.—Diagram showing the position of the crystallites in polyethylene terephthalate crystallized at 239° C.

FIG. 13.—Diagram showing the position of the crystallites in polyethylene terephthalate crystallized at 220° C.

point, on the other hand, at which the conditions of equilibrium are more nearly attained, it would seem that other factors may come into play, though we do not know for certain what these factors are. Possibly the reduction in volume by a few per cent which takes place during crystallization may exert some influence. Moreover, shrinkage is not equal perpendicular to a crystallite in all directions. Other likely factors are the viscosity and heat of fusion of the polymer, the pliability of the molecules, and the shape of the crystallites.

THE CRYSTALLIZATION OF NATURAL RUBBER

Natural rubber is one of the most thoroughly studied of all crystallizing polymers and it is, therefore, with reference to natural rubber that the correlation of the autoörientation mechanism with published investigations will be discussed.

(1) Typical S-shaped curves are invariably found if the quantity of crystalline material in natural rubber is plotted against time. This means to say that crystallization consists of an induction period, a period of increasing

crystallization velocity up to a constant value, and finally a slowing-down, owing to depletion of the quantity of amorphous material. Russell[16] wanted to measure separately the speed of nucleus formation and that of nuclear growth, but found that the product of maximal rate of crystallization and induction period was virtually constant. From this Russell inferred that there must be a common factor which affected both nuclear growth and the formation of nuclei. The autoörientation mechanism implies that nuclear growth results in the generation of nuclei; hence, with increasing rate of crystallization, the formation of nuclei is accelerated and, consequently, the induction period is shortened. In the result, the product of the maximal rate of crystallization and the induction period becomes approximately constant.

(2) Bekkedahl and Wood[17] state that the lower limit of the melting range of rubber is higher by about 5° C than the temperature at which the rubber crystallizes. If the rubber is crystallized at higher temperature (20° C), this difference in temperature increases to as much as roughly 10° C.

The explanation for this is that the first crystallites are formed in wholly amorphous rubber. The crystallites formed subsequently balance the tensions set up by the first crystallites, so that ultimately a structure results with far less tension. Hence the crystallites stabilize each other and, as a result, the melting point is eventually raised. It will be evident that the more completely the tensions cancel each other out, so much the greater will be this effect. That is why a greater difference of temperature is found at higher temperature. At the same time we now know why a rubber always crystallizes under conditions of nonequilibrium.

The fact that the size of the range of melting temperatures remains approximately constant fits into this picture remarkably well. The better the tensions are balanced and the greater the mutual stabilizing effect of the crystallites, so much the higher will be the end melting point.

(3) Rubber in latex does not crystallize, as Bekkedahl[18] was the first to show. This was investigated further by van Amerongen[19]. A latex of 60 per cent rubber content was stabilized with a nonionogenic emulsifier. Enough sulphuric acid was then added to transform the water phase into sulfuric acid of 30 per cent. This acid does not alter the chemical constitution of the rubber.

It was then found dilatometrically that, at −15° C, no crystallization had taken place at the end of three weeks. On the contrary, dry rubber crystallizes at this temperature in a few hours.

Hitherto, no satisfactory explanation had been advanced to account for this, but the answer is not too far to seek if the relation between the size of a spherulite and of a latex particle is considered. The diameter of latex particles is at most 2 microns, whereas spherulites easily attain a size of 50 microns. Thus spherulites have a volume thousands of times larger than that of latex particles. Admittedly, one individual latex particle may crystallize if by chance a nucleus is formed in it, but this does not affect the nuclear formation in other particles. The autocatalytic character of the crystallization is, therefore, lost and the induction period is considerably lengthened. This is the cause of the enormous retardation of crystallization in latex.

From this view it may be assumed that a polymer will not crystallize if it is so finely divided that there is little likelihood of nuclear formation in an individual particle.

(4) Treloar[15] found that, contrary to observations made on thin films made from solution, the rate of crystallization of a film from latex is not very

reproducible. This, too, can be explained if it be assumed that the individuality of the latex particles is somewhat preserved during film forming, owing to which the mechanism of crystallization is interrupted, though less so than in the original latex.

It will be clear from the foregoing that the conception of autoörientation mechanism helps to explain several phenomena that happen during the crystallization of natural rubber and to coordinate them. In a qualitative sense, other high polymers resemble natural rubber in many respects, but on the whole we know less about them.

SYNOPSIS

In this article a concept of the mechanism of crystallization is given, on the basis of which, the origin of spherulites may be explained. A tentative explanation of several related phenomena is based on the new concept. Crystallites are conceived to be small collections of strongly oriented polymer which, on fusing, exhibit marked shrinking in the direction of orientation. Particles of amorphous material therefore stretch out in a certain direction during crystallization, as the result of which there is substantial contraction in the other directions. This is termed autoörientation. As the growing crystallite has to be fed from surrounding material, an orientation is initiated in the latter at right angles to the first crystallite. As a result of this orientation, crystallites are formed there which are oriented perpendicular to the first crystallite. In their turn, these crystallites induce orientation in the surroundings, and in this way crystallization becomes autocatalytic in character. Spherulites owe their origin to the fact that the various sectors in a symmetrical spherical order mutually cancel out their stretching and shrinking tendencies. In highly crystalline polymers with rapid nuclear formation, there first comes into existence numerous randomly oriented nuclei, which proliferate to small crystallites. Wherever these small crystallites come to be arranged in a suitable position, their relative tensions are cancelled out and they grow into a spherulite. Simultaneously small crystallites which are in an unfavorable position are consumed by the growing spherulite, or else oriented in the correct direction and incorporated. As spherulites commonly measure from 10 to 50 microns, compensation between the tensions of the various sectors has to take place at long distances. At higher temperatures, compensation is, as a rule, found at short distances, i.e., crystallites which are at right angles to each other are in close proximity. Therefore spherulites varying individually come into existence as the crystallites are subject to other influences in addition to autoörientation. At very low temperatures the primary small crystallites are too stable to develop into spherulites. The mechanism of crystallization as thus conceived implies that the melting point of a polymer depends, not only on the dimensions and perfection of the crystallites, but also on the specific arrangement of the crystallites, i.e., the degree to which they stabilize each other by mutual compensation of tensions. It also helps to explain the following facts which have been noted in experiments performed with natural rubber: (1) The typical S-shape of the crystallization curve and the constancy of the product of induction period and maximum rate of crystallization. (2) The fact that natural rubber always crystallizes under nonequilibrium conditions. (3) The failure of rubber in latex to crystallize and the fact that the rate of crystallization in films produced from latex is poorly reproducible.

ACKNOWLEDGMENTS

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REFERENCES

[1] Wallner, *Monatsh.* **79**, 87, 279 (1948).
[2] Hoffmann, *J. Am. Chem. Soc.* **74**, 1696 (1952).
[3] Buckley, Cross, and Ray, *J. Chem. Soc.* **1950**, p. 2714.
[4] Bunn and Alcock, *Trans. Faraday Soc.* **41**, 317 (1945).
[5] Kirchhof, *Kautschuk* **5**, 175 (1929).
[6] Smith and Saylor, RUBBER CHEM. & TECHNOL. **12**, 18 (1939).
[7] Price, *J. Am. Chem. Soc.* **74**, 311 (1952).
[8] Gabler, *Naturwissenschaften* **35**, 284 (1948).
[9] Jenckel and Wilsing, *Z. Elektrochem.* **53**, 4 (1949).
[10] Keller, *Nature* **169**, 913 (1952).
[11] Schuur, G., unpublished results.
[12] Roseveare, Waller, and Wilson, *Textile Research J.* **18**, 114 (1948).
[13] Park, RUBBER CHEM. & TECHNOL. **12**, 778 (1939).
[14] Reinhardt, *Ind. Eng. Chem.* **35**, 422 (1943).
[15] Treloar, RUBBER CHEM. & TECHNOL. **15**, 251 (1942).
[16] Russell, *Trans. Faraday Soc.* **47**, 539 (1951).
[17] Bekkedahl and Wood, *J. Chem. Physics* **9**, 193 (1941); RUBBER CHEM. & TECHNOL. **14**, 544 (1941).
[18] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); RUBBER CHEM. & TECHNOL. **8**, 5 (1935).
[19] Van Amerongen, G. I., private communication.

MECHANICAL INVESTIGATIONS OF ELASTOMERS IN A WIDE RANGE OF FREQUENCIES *

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INTRODUCTION

Many experimental investigations have shown that plastics in general, as well as elastomers and their solutions, do not behave like Newtonian liquids. They both have viscosity and elasticity, the combination of which, according to the Maxwell postulate, causes their properties to be dependent on time, and leads us to call them viscoelastic bodies. This dependence does not exist, either for the Newtonian liquid whose mechanical properties are determined by its viscosity, or for the elastic body whose properties are determined by its elasticity. The time element introduces a peculiar difficulty in measuring the mechanical properties of these substances. Whereas the well-known Maxwell body describes this time dependence in simple mathematical expressions, it does not apply to the experimental results. The properties of viscoelastic bodies are not described by a Maxwellian body, but rather by a distribution of an infinite number of Maxwellian bodies, each having a so-called relaxation time.

The existence of this infinite distribution calls imperatively for an investigation of the properties of these viscoelastic bodies in as wide a range of frequencies or times as possible in order to define them. Most investigators have used one method in a range of frequencies no wider than about 1 to 100. This range can be extended by using the observation of Ferry[1] that the properties of viscoelastic bodies investigated at different temperatures, in the case of dynamic investigations with sinusoidal vibrations, seem to be described by shifting one standard curve on the frequency axis. One can superimpose measurements at different temperatures and extend the range of frequencies to about 1 to 1,000,000. But using Ferry's method of reduced variables necessitates some assumptions that, though very probable, have as yet not been proven exactly by experiments. It therefore seemed important to have a method for investigating the mechanical properties of viscoelastic bodies in a frequency range of about 1 to 1,000,000 under isothermal conditions. This paper describes a basic method and the results obtained for several elastomers.

PRINCIPLES OF OPERATION

In order to measure the viscosity and elasticity of viscoelastic bodies in a wide range of frequencies, it is profitable to use an arrangement that allows the frequency alone to be changed, while using one sample throughout the investigation. It is well known that the size of the sample affects the pure geometry of mechanical strains for higher degrees of deformation and that the geometry

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is not always exactly known. Using a single specimen, we at least know that the geometric corrections are constant throughout the investigation, even if they influence the absolute values measured. This degree of incertitude is not extremely important; the mechanical constants of viscoelastic bodies always vary within a certain range due already to some variation in composition or molecular weight, and cannot be considered as absolute physical constants of the substance like density, etc.

At the start of this investigation it was deemed important to work with forces and deformations not infinitely small, but in the range of those encountered in practice. This is also important should one want to investigate the nonlinear mechanical properties of viscoelastic bodies. Simple shear gives the most linear relationships of all the methods of stressing, especially with elastomers which allow a high degree of elongation. Furthermore, stresses in simple shear are nearly uniform throughout the sample.

To investigate elastomers in a wide range of frequencies, we can use the stress-relaxation method or an investigation under cyclical vibrations. The stress-relaxation method as used by Tobolsky and his associates[2] allows a practically infinite range of times, but it gives only one quantity: the time-dependent modulus of elasticity. An investigation with cyclical vibrations allows us to measure two quantities: the dynamic modulus of elasticity, and a quantity proportional to the losses of the system. This latter can be described as the viscosity, η, or the imaginary part of the shear modulus of elasticity, $\eta \times \omega$, where ω is the circular frequency of the vibrations. In the case of deformational shear vibrations, the quantities are the dynamic shear modulus G' and the dynamic loss modulus $G'' = \omega\eta$. Using vibrations in a wide range of frequencies practically eliminates resonance methods, because the resonant frequency depends on the square of the mass for a constant sample, and a frequency variation of 1 to 1,000,000 would require a variation of the mass of 1 to 10^{-12}. We therefore selected a nonresonant method. From the discussion of reduced variables, it is clear that in the investigation of elastomers it is not the value of the frequencies but the range of frequencies that is important.

These basic principles of operation are (1) large range of frequencies, (2) large deformations or forces, and (3) nonresonant method—lead us to the method of the hysteresis loop, i.e., the dependence of deformation on the force for harmonic shear vibrations. The method has been used by several investigators beginning with Schmidt[3] in 1923.

SAMPLE

The sample consists of two $1 \times 1 \times \frac{1}{4}$ inch pieces of the material to be investigated, sandwiched between three brass plates $1\frac{1}{4} \times 1\frac{1}{2} \times \frac{3}{8}$ inch. The bond between the sample and the plates, in the case of filled rubber, is formed by vulcanization. In the case of soft rubber, polyvinyl chloride and Thiokol, the adhesion is so poor that a suitable cement had to be used. The corrections to the calculated values for the finite size of the sample, using formulas for an infinite sample, are about 5 per cent according to Read[4]. The maximum double amplitude used was about 1000 microns, or about 8 per cent maximum deformation.

The middle plate of the sample sandwich was mounted in a frame connected through a dynamometer to a reciprocating part, which gave the sinusoidal motion, whereas the two other plates were solidly clamped to the machine. It is obviously a stressing under simple shear.

METHOD OF STRESSING

Stresses are provided by an adjustable double cam with a throw between 0 and 4000 microns double amplitude, which could be driven between 13 and 0.000006 cps, giving a range of slightly over 1 to 2,000,000 in frequency. Beyond 13 cps, the system began to be mechanically unstable (unwanted resonant frequencies being excited), whereas the lower frequencies required such long times as to be inconvenient. All the bearings were sleeve bearings, rather than ball or roller bearings, to eliminate any possible periodic disturbance. The sample was placed in a liquid bath that could be electrically heated up to 75° C or cooled in a cold room to −30° C. Results reported here were obtained at room temperature (about 25° C or 77° F) without using the temperature control.

SENSITIVE ELEMENTS

The force was measured by a dynamometer between the driving member and the frame carrying the sample. The deformation of a steel ring was measured by a Schaevitz (type 040) linear-variable differential transformer. The movement of the frame was picked up by a second linear-variable differential transformer, type 080. The range of forces with one dynamometer was between a few grams and 10 kilograms double amplitude. The range of deformations was between 10 and 1000 microns double amplitude. This gives a very great range of measurable viscosities, amounting to about 1 to 1,000,000, i.e., from 10^6 to 10^{12} poises.

ELECTRONIC EQUIPMENT

Both differential transformers were excited by a 4 volt, 1600 cycle, stabilized frequency generator. The output of each differential transformer after passing the gain control was amplified and rectified through a phase sensitive bridge and low-frequency bypass filter in the usual manner. Both circuits were entirely symmetrical so that the electronics did not introduce any amplitude or phase errors in the range of frequencies investigated. The outputs of the filters were fed to the x and y plates of a Du Mont 304-*H* oscilloscope and photographed by a Du Mont land camera. The amplitudes of the axes were regulated by the gain control, using the amplifiers at constant output, so that the trace could be well measurable on the oscilloscope screen. Absolute measurements were made possible by using a switch step potentiometer (attenuator) excited by the same voltage as the transformers, which was directly calibrated in kilograms and microns by putting on loads or motions in the instrument and comparing them to the electrical amplitudes determined by the attenuator. Motion at various frequencies was produced by a synchronous motor of 3600 rpm, which drove the cam through a series of pulleys and worm-gear boxes. The low frequencies were calculated from the known gear ratios and the higher frequencies were measured by stop watch and revolution counter.

GENERAL ASSEMBLY

The specimen holder with the cam and the sensitive elements, together with the temperature bath, were mounted on a 1600-pound cement block, which itself was isolated by steel springs from a concrete pier sunk into the ground. The electronic equipment, the worm drives and other gears were shock-mounted on a table and only connected with the instrument by a rubber v-belt,

thus eliminating the transmission of disturbing frequencies during the measurement as far as possible. This was important, especially in measuring over long times or measuring very stiff substances with only a few microns double amplitude or very low forces below 100 grams. The temperature bath was heated by an immersion heating element and cooled by a copper coil with water.

RESULTS

Figures 1 through 4 give the results for a number of elastomers. Figure 1 summarizes the results for the National Bureau of Standards sample of polyisobutylene that had been investigated by a number of laboratories. Our values amplify the frequency range by about two decades at the lower end, and especially important is the strongly defined minimum of the loss angle *vs* fre-

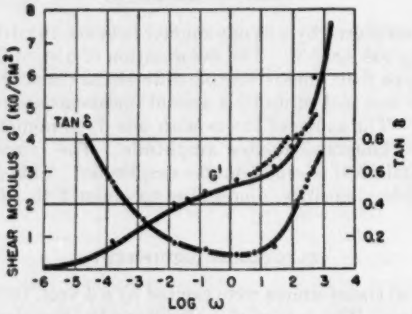

FIG. 1.—Frequency dependence of G' and tan δ for polyisobutylene at 25° C. G' is the dynamic shear modulus; δ is the loss angle.

quency. The values are concordant with the ones obtained by stress relaxation or by other methods. The rise of the loss angle with diminishing frequency indicates that at some still lower frequency the polyisobutylene will behave as a Newtonian liquid, i.e., it will flow with a constant viscosity.

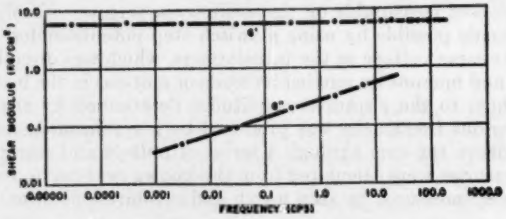

FIG. 2.—Frequency dependence of shear modulus, natural gum rubber. G' is the dynamic shear modulus; G'' is the dynamic shear loss modulus.

Figure 2 shows the measurements on vulcanized rubber gum. The values obtained by Nolle[6] at high frequencies for a similar composition of rubber gum are concordant, so that, with the combination of both methods, a continuous range of values from 0.000006 to about 5000 cycles is available. The moduli of elasticity measured by Nolle were divided by three to be compared with the

shear modulus measured in this work. The losses of gum rubber are very similar to these of Nolle, except for the absence of a sharp downward trend that he obtained, which was probably at the limit of application of his methods. The losses at low frequencies, below 0.003 cps, could not be measured; the gum rubber below these frequencies behaved like an ideal elastic body with losses well below 1 per cent.

FIG. 3.—Natural rubber—tread stock. G' is the dynamic shear modulus; G'' is the dynamic shear loss modulus.

Figures 3 and 4 show the results for a natural-rubber tread and a cold-rubber tread stock[6]. Both the modulus and the losses are frequency-dependent. Values in the higher frequency range were obtained by putting our specimen in a Gehman[7] tester, where it was stressed in exactly the same way: simple shear. Figure 5 presents the results for a blend of Thiokol[8] and shows at 25° C essenti-

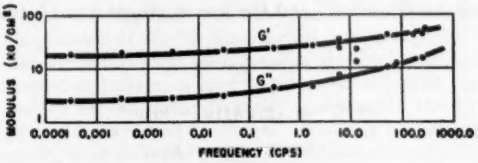

FIG. 4.—Cold rubber—tread stock. G' is the dynamic shear modulus; G'' is the dynamic shear loss modulus.

ally the same behavior as other elastomers. At higher temperatures Tobolsky and Stern[9] have obtained a behavior very similar to that of Maxwellian bodies. This is definitely not the case at 25° C.

Measurements of the properties of the viscoelastic bodies at different amplitudes of vibration showed that apparently the amplitude does not influence

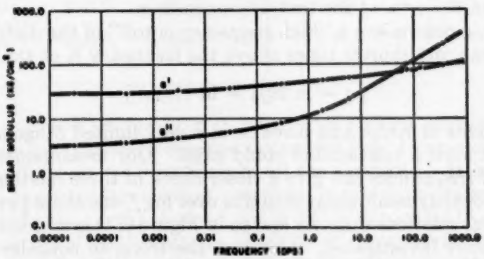

FIG. 5.—Frequency dependence of shear modulus, Thiokol H-5. G' is the dynamic shear modulus; G'' is the dynamic shear loss modulus.

the viscosity to any measurable extent beyond the inherent error limit of the machine. The modulus G' and $\tan \delta = G''/G'$ have possibly a small amplitude dependence, resulting in the modulus being smaller at higher amplitudes and $\tan \delta$ increasing, but the effects are comparatively very small, especially considering the influence of frequency on these properties. It is interesting to note that if viscosity, which in itself is frequency dependent, does not appreciably depend on amplitude, then it is not the rate of shear that causes changes but rather the frequency that is the most important factor in determining the viscosity of elastomers.

DISCUSSION

All the experimental curves except the one for the shear modulus of natural gum rubber are frequency dependent. They are extremely flat in a frequency range of at least $1:10^6$. This substantiates very well the difficulties of investigating viscoelastic bodies mentioned in the introduction. For similar curves, Kuhn and Kuenzle[10] in 1946 developed a theory that was subsequently called "box distribution"; they assumed that the probability of a partial shear modulus $dG'/d\tau$ for a mechanism with a relaxation time τ was

$$dG'/d \ln \tau = b/a^2 = \text{const.}$$

This idea, after adequate mathematical treatment modifying somewhat the original formulas, led to the following expressions for the frequency dependence of dynamic modulus G' and G'' and the loss angle $\cot \delta = G'/G''$:

$$\frac{1}{G'} = \frac{a - \ln \omega}{b} \tag{1}$$

$$1/G'' = (2/\pi b)(a - \ln \omega)^2 \tag{2}$$

$$\cot \delta = (2/\pi)(a - \ln \omega) \tag{3}$$

These formulas are valid under the simplifying assumption

$$X = \frac{\pi^2}{(a - \ln \omega)^2} \ll 1$$

In Kuhn's case this was true to a large extent. But in some of our samples this was not the case. We have, therefore, calculated the second approximation of the formulas for values $0 < x < 1$. The first approximation is valid until $x \leqq 0.3$ with an error of 10 per cent. For higher values of x, the $1/G'$ values are higher than the ones of the first approximation.

Physically, a determines a "high frequency cutoff" of the distribution function, eliminating any shorter times above the frequency f_0 or time τ_0:

$$[a = \ln 2\pi f_0 = \ln (1/\tau_0)]$$

Measurements of Kuhn and Kuenzle in a very limited range of frequencies indicated that such a relationship could exist. Our measurement in a much wider range of frequencies can give a closer check of these relations. By plotting the reciprocal dynamic shear modulus over $\log f$, one should expect, according to (1), linear relationship. As is seen in Figure 6, this is indeed the case for all the elastomers investigated. One has, therefore, to consider the assumptions made by Kuhn as to the distribution of the relaxation times to be valid for these elastomers in an extremely wide range of frequencies. This is not the

case for the polyisobutylene, which at very low frequencies approaches the behavior of a liquid.

The validity of the relationships of Kuhn leads to unexpected results. Under no condition can the "true value" of the static shear modulus of an elastomer be found, since the dependence on the logarithm of the frequency does not warrant a limiting value at any frequency. There are not yet any indications that this statement could be modified for a range of frequencies

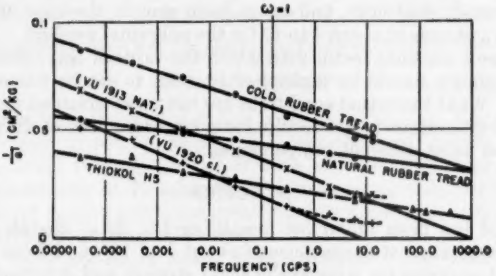

FIG. 6.—Plot of $1/G'$ vs. $\log f$ to test the Kuhn equations.

above or below the one investigated. Of course some limitation as to the limits of the validity of Equations (1) to (3) should exist, but in any case in the lower frequency range no deviations have been found. At the lowest frequencies investigated, the elastomers behave neither as pure elastic bodies nor Newtonian liquids. The viscosity as calculated from G'' has roughly the hyperbolic dependence on frequency as expected by Kuhn. There is no particular value of viscosity and elasticity that could be assigned to the elastomer except, perhaps,

TABLE I

Sample	$\frac{1}{G'}$ at $\omega=1$ (cm.²/kg.)	$\frac{1}{G'}$ at 10^{-5} cps (cm.²/kg.)	b (kg./cm.²)	a —	τ_0 (sec.)	f_0 (cps)
Natural-rubber tread	0.0430	0.0570	691.2	29.71	1.25×10^{-13}	1.628×10^{12}
Cold-rubber tread	0.0603	0.0928	267.0	16.02	1.100×10^{-7}	1.151×10^{6}
Thiokol	0.0240	0.0405	586.5	14.06	7.82×10^{-7}	1.943×10^{5}
Polyvinyl chloride *VU* 1913 natural	0.0345	0.0733	250.0	8.625	1.8×10^{-4}	8.95×10^{2}
Polyvinyl chloride *VU* 1920 clear	0.0173	0.0600	226.0	3.91	2.0×10^{-2}	7.95

the one at $\omega = 1$ ($f = 0.159$ cps or $\ln \omega = 0$). For Kuhn's relationships to be valid further requires that the properties depend on only two constants, a and b, that occur in different combinations in all the formulas. It is essentially immaterial which particular method one uses in order to determine these constants. This fact is very important, for it makes it possible to describe the viscoelastic properties of elastomers, for which the Kuhn relations hold, by only two constants. A tabulation of these constants for our elastomers is given in Table I.

The practical value of the results obtained by this investigation is obvious. Because the mechanical constants of elastomers depend so much on the frequency of stress, it is clear that one has to measure these constants at the same frequencies that occur in practice; i.e., if the elastomer is to be used in shock absorbers, the elastic constants have to be measured at frequencies between roughly 3 and 50 cps. Should the application be in gaskets under steady load, measurements at very low frequencies, such as 1 cycle per day, are necessary. The susceptibility of the mechanical properties to changing frequency are different for each elastomer, and range from zero in the case of natural gum rubber up to a change of about 1 to 10 for the polyvinyl product. Thus it is not possible to use a constant factor with which the value of (say) shear modulus at any one frequency should be multiplied in order to get its value at any other frequency. What the actual conditions are can be ascertained only by expanding these investigations to get results for a larger number of different plastics, probably also using different temperatures.

SYNOPSIS

A method has been found for measuring the shear moduli and losses of elastomers in a range of frequencies of about 1 to 10^6, and from 10 cps down. This method provides for large cyclic shear stresses and deformations without employing resonance methods. Only one sample is needed for the complete study, the frequency of stress being the only variable. The method gives results that fit the "box-distribution function" developed by Kuhn and Kuenzle. Results for a series of elastomers show that such investigations are important in ascertaining the mechanical properties of elastomers in practice.

REFERENCES

[1] Ferry, Fitzgerald, Grandine, and Williams, *Ind. Eng. Chem.* **44**, 703 (1952).
[2] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944).
[3] Schmidt, *Gesundh. Ing.* **46**, 61 (1923).
[4] Read, *J. Applied Mech.* **17**, 349 (1950).
[5] Nolle, *J. Polymer Sci.* **5**, 1 (1950).
[6] These were prepared by the Rubber Section of the National Bureau of Standards.
[7] Gehman, Woodford, and Stambaugh, *Ind. Eng. Chem.* **33**, 1032 (1941).
[8] The Thiokol was Type H-5, and was obtained from the Thiokol Corporation, Trenton, New Jersey.
[9] Tobolsky and Stern, *J. Chem. Physics* **14**, 93 (1946).
[10] Kuhn and Kuenzle, *Helv. Chim. Acta* **30**, 307, 464 (1947).

STUDY OF THE VISCOELASTIC BEHAVIOR AND MOLECULAR WEIGHT DISTRIBUTION OF POLYISOBUTYLENE*

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INTRODUCTION

The viscoelastic behavior of linear high polymers has commanded considerable attention in recent years. The very thorough studies by Fox and Flory[1] of the melt viscosity of polystyrene and polyisobutylene, the stress relaxation experiments of Tobolsky and coworkers[2], and dynamic-mechanical studies by Ferry[3] have contributed greatly to our knowledge of the mechanical behavior of these interesting substances.

However, there are many facets of this subject which have not received thorough experimental investigation. In particular, there has been no detailed study of the effect of molecular weight and polydispersity on the elastic behavior of viscoelastic materials. It was felt, therefore, that a study of the viscoelastic behavior of a series of very carefully characterized samples of a representative linear high polymer would contribute substantially to the understanding of this subject. The polymer chosen was polyisobutylene, which displays both flow and elastic behavior at room temperatures.

PREPARATION OF POLYISOBUTYLENES

The polyisobutylenes used were prepared from three whole polymers[4], and in order to obtain a series of polymers of varying degrees of polydispersity (that is, both narrow and broad molecular weight distributions) part of each whole polymer was fractionated, using fractional precipitation by acetone from 2 per cent solutions in benzene, as described by Fox and Flory[5]. The precipitated samples were dried to constant weight in vacuo at 70° C. The fractionation scheme is best described by Table I.

Several comments may be made regarding Table I. In order to obtain as much variation in polydispersity as possible, only a few fractions of each material were taken; some of these were then refractionated. Since so few fractions would be of little use in calculating a molecular-weight distribution, no attempt to accurately measure the amount of material was made.

The capital letters in parentheses in Table I are the code letters which will henceforth be used to identify the samples. This code makes no distinction between "whole polymers" and "fractions," which would only be misleading in a fractionation of this sort. Indeed, as will be subsequently shown, many of the "fractions" are quite polydisperse.

The numbering of the polyisobutylenes is, generally, in the order of increasing molecular weight.

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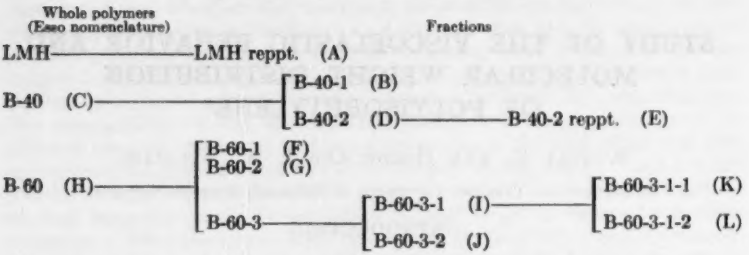
TABLE I

FRACTIONATION OF POLYISOBUTYLENES



CHARACTERIZATION OF POLYISOBUTYLENES

Ideally, the characterization of a polydisperse high polymer would include, in addition to a precise chemical analysis of the material, an exact knowledge of its molecular-weight distribution. While the latter is very difficult, if not impossible to attain at the present time, any experimental technique or techniques which yield several average molecular weights will give some information as to the general shape of the distribution function. Sedimentation equilibrium is a method admirably suited to this problem, in that each experiment yields three, and sometimes more, average molecular weights. We do not propose to discuss here the general theory of sedimentation equilibrium; the reader is referred to the extensive literature on the subject, particularly the treatise of Svedberg and Pederson[6], and the series of papers by Wales and coworkers[7].

In order to use the sedimentation equilibrium method to characterize the polyisobutylene samples, it was first necessary to select a suitable solvent and determine several constants for this solvent–solute system. The solvent chosen was 2,2,4-trimethylpentane, more commonly known as isooctane. Three liters of isooctane[8] were redistilled through an 18-plate column, and the fraction boiling between 98.0 and 98.2° C at 720 mm. was retained.

PARTIAL SPECIFIC VOLUME

Since the sedimentation of a macromolecular solute depends on the partial specific volume of that solute in the solvent used, it was necessary to determine this quantity for polyisobutylene in isooctane. The partial specific volume was obtained from measurements at 25.00 ± 0.01° C, of the density of the solvent and two solutions, one containing 0.004568 g./g. of polymer C, the other containing 0.007002 g./g. of polymer H. These measurements were made in a capillary pycnometer fashioned from a 25-cc. Erlenmeyer flask. All weighings were with calibrated weights, and air buoyancy and vapor corrections were made. The density of pure isooctane at the above temperature was found to be 0.6875 g./cc., in good agreement with the best literature value[9] of 0.6877 g./cc. The apparent partial specific volumes obtained from the two experiments were 1.053 cc./g. and 1.060 cc./g., respectively. Excluding the unlikely possibility of exactly compensating variations of the partial specific volume with molecular weight and concentration the apparent partial specific volume would seem to be independent of these two variables, at least

in the range covered. Accordingly the partial specific volume of polyisobutylene in isooctane at 25.0° C was taken to be 1.059 in subsequent calculations.

SPECIFIC REFRACTIVE INDEX INCREMENT

Since a refractometric method (the Lamm scale method) was used to measure concentration gradients in the ultracentrifuge cell, it was necessary to determine the specific refractive index increment, dn/dc, for polyisobutylene in isooctane at 25.0° C. This was accomplished with the aid of a simple but sensitive differential refractometer. A glass scale, illuminated by monochromatic light (Hg green line), was photographed through a cubical glass cell. This cell was divided into two compartments by a diagonal glass partition. Photographs were taken, first, with both compartments filled with solvent, and then with one filled with solvent, the other with solution. The

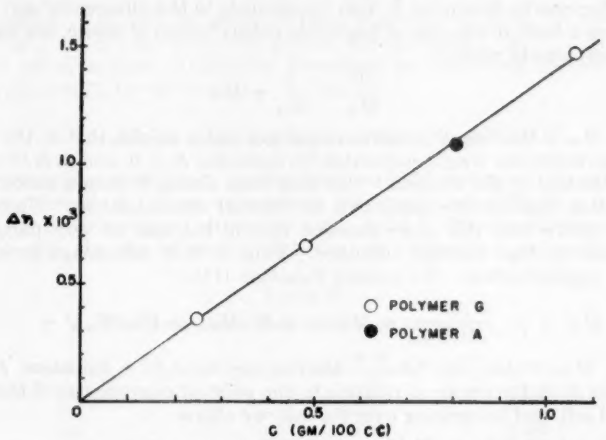


FIG. 1.—Δn *vs.* C for polyisobutylene in isooctane.

displacements of scale lines in the solution picture as compared to the reference picture can be shown to be very nearly proportional to the difference in refractive index between solution and solvent. These displacements were measured with a Gaertner microcomparator, with a precision of ± 0.0002 cm., which corresponds to a difference of ± 0.00001 in the refractive index increment.

All measurements were made at 25.0 $\pm$ 0.1° C, the cell being enclosed in an air thermostat. The instrument was calibrated with solutions of reagent grade sucrose, for which the specific refractive index increment is very accurately known[10]. The refractive index increments of four solutions were measured, three of polymer G and one of polymer A. The results are shown in Figure 1. A single straight line passes through all of the points, within experimental error; the slope of this line gives a value for the specific refractive index increment of polyisobutylene in isooctane at 25° C of 0.00139 (g./100 cc.)$^{-1}$, apparently independent of both molecular weight and concentration.

THE NON-IDEALITY CORRECTION

In the theory of sedimentation equilibrium for a nonideal solute, as developed by Wales[11], a correction is made for the deviation from Raoult's law of the high polymer–solvent system in the ultracentrifuge cell. This correction appears as the coefficient B in Wales' fundamental equation for the weight-average molecular weight at the point x in the cell:

$$M_{wx} = \frac{dc_x/dx}{c_x(2Ax - Bdc_x/dx)} \tag{1}$$

where x = distance from center of rotation, c_x = concentration at point x, $2A = (1 - \bar{V}\rho)\omega^2/RT$, $\bar{V}$ = partial specific volume of solute, ρ = density of the solution, and ω = angular velocity of the rotor.

It has been shown[12] that the coefficient B is the same quantity which determines the concentration dependence of osmotic pressure and light scattering; in fact, these methods can be used to measure B. However, it would be advantageous to determine B from experiments in the ultracentrifuge; Wales[13] has shown that, in the case of negligible redistribution of solute, one can write the approximate relation:

$$\frac{1}{M_{wi}} = \frac{1}{M_w} + Bc_0 \tag{2}$$

where M_{wi} is the "ideal" weight-average molecular weight, that is, the weight-average molecular weight calculated by assuming $B = 0$, and c_0 is the overall concentration of the solution. One may thus obtain B from a series of sedimentation equilibrium experiments at different concentrations. However, as Wales points out, this approximation fails in the case of very polydisperse materials or high angular velocities. Thus it is of advantage to obtain a better approximation. We rewrite Equation (1):

$$M_{wx} = \frac{M_{wix}}{1 - Bc_xM_{wix}} = M_{wix}(1 + Bc_xM_{wix} + B^2c_x^2M_{wix}^2 + \ldots) \tag{3}$$

where $M_{wix} = (dc_x/dx)/2Axc_x$. Multiplying by $c_x(x + \delta)$, where δ is the distance from the center of rotation to the point of convergence of the sector-shaped cell, and integrating over the cell, we obtain:

$$\int_a^b M_{wx}c_x(x + \delta)dx = \int_a^b M_{wix}c_x(x + \delta)dx + B\int_a^b M_{wix}^2c_x^2(x + \delta)dx + \ldots \tag{4}$$

where a and b represent the ends of the solution column. The weight-average molecular weight of the solute in terms of M_{wx} is given by [11]:

$$M_w = \frac{\int_a^b M_{wx}c_x(x + \delta)dx}{\int_a^b c_x(x + \delta)dx} = \frac{\int^b M_{wx}c_x(x + \delta)dx}{c_0\int_a^b (x + \delta)dx} \tag{5}$$

Using this equation and rearranging, we obtain:

$$\frac{1}{M_{wi}} = \frac{1}{M_w} + \frac{B}{(M_{wi})^2}\frac{\int_a^b M_{wix}^2c_x^2(x + \delta)dx}{\int_a^b c_x(x + \delta)dx} \times \left\{\frac{1 + B\dfrac{\int_a^b M_{wix}^3c_x^3(x + \delta)dx}{\int_a^b M_{wix}^2c_x^2(x + \delta)dx} + \ldots}{1 + B\dfrac{\int_a^b M_{wix}^2c_x^2(x + \delta)dx}{\int_a^b M_{wix}c_x(x + \delta)dx} + \ldots}\right\} \tag{6}$$

Now the term in brackets will be very nearly equal to one. Then:

$$\frac{1}{M_{wi}} \cong \frac{1}{M_w} + \frac{B}{(M_{wi})^2} \frac{\int_a^b M_{wix}^2 c_x^2 (x+\delta)dx}{\int_a^b c_x (x+\delta)dx}$$

$$= \frac{1}{M_w} + Bc_0 \frac{[\int_a^b M_{wix}^2 c_x^2 (x+\delta)dx][\int_a^b (x+\delta)dx]}{[\int_a^b M_{wix} c_x (x+\delta)dx]^2} \quad (7)$$

or:

$$\frac{1}{M_{wi}} = \frac{1}{M_w} + Bc_0^* \quad (8)$$

where:

$$c_0^* = c_0 \frac{[\int_a^b M_{wix}^2 c_x^2 (x+\delta)dx][\int_a^b (x+\delta)dx]}{[\int_a^b M_{wix} c_x (x+\delta)dx]^2} \quad (9)$$

The quotient c_0^*/c_0 can be obtained from experimental data. If one then plots $1/M_{wi}$ vs. c_0^*, the slope will give B, the intercept $1/M_w$. This would seem to afford a more satisfactory procedure for correcting sedimentation equilibrium results for nonideality.

SEDIMENTATION EQUILIBRIUM EXPERIMENTS

Sedimentation equilibrium studies were made of several of the polymers previously described. These experiments were performed at 25.00 ± 0.02° C, using a Svedberg low-speed ultracentrifuge. A list of the experiments is given in Table II. It was observed that the high-molecular polyisobutylenes

TABLE II

SEDIMENTATION EQUILIBRIUM EXPERIMENTS

Experiment	Polymer	Angular velocity, r.p.m.	c_0, g./100 cc.
188	E	4400	0.307
189	E	4500	0.148
190	E	4720	0.466
191	B	4360	0.202
194	A	7780	0.203
195	J	3510	0.140
196	I	3500	0.241
198	F	3640	0.228
199	H	3600	0.180
208	K	3610	0.241

approached equilibrium quite slowly; indeed, in experiment 195 (polymer J, $M_v = 14.7 \times 10^5$) equilibrium was not reached in 14 days. In all other cases, equilibrium was definitely attained.

RESULTS

The three sedimentation equilibrium experiments with polymer E were used to calculate the nonideality correction B for the system polyisobutylene–isooctane. The results of this calculation are presented in Table III and Figure 2.

The slope of the plot of $1/M_{wi}$ vs. c_0^* in Figure 2 yields a value for B of 5.4×10^{-6}. Actually, a trial and error calculation shows this to be a slight overcorrection; the value 5.1×10^{-6} gives average molecular weights more nearly independent of concentration. These values are given in the last three columns in Table III, and the $1/M_w$ values thus obtained are shown as the lower curve in Figure 2. This result (5.0×10^{-6}) is in fair agreement with

TABLE III

NONIDEALITY CORRECTION FOR POLYISOBUTYLENE IN ISOOCTANE

Expt.	g./100 c.c. c_0	g./100 c.c. c_0^*	$M_{wi} \times 10^{-5}$	$M_w \times 10^{-5}$	$M_z \times 10^{-5}$	$M_{z+1} \times 10^{-5}$
188	0.307	0.405	2.73	7.80	13.2	18.0
189	0.148	0.251	3.55	7.01	11.8	18.0
190	0.466	0.551	2.25	7.69	12.4	20.0
Average				*7.50*	*12.4*	*18.7*

that from a single light scattering experiment with polymer A (4.3×10^{-6}) and a previously reported result[14] for a very high molecular-weight polyisobutylene (5.6×10^{-6}). Previous experiments[15] with a whole polymer did not yield a constant value of B; this is now believed to be a result of the extreme polydispersity of this material. A comparison of the former ultracentrifuge method for determining B is shown by the dotted line in Figure 2.

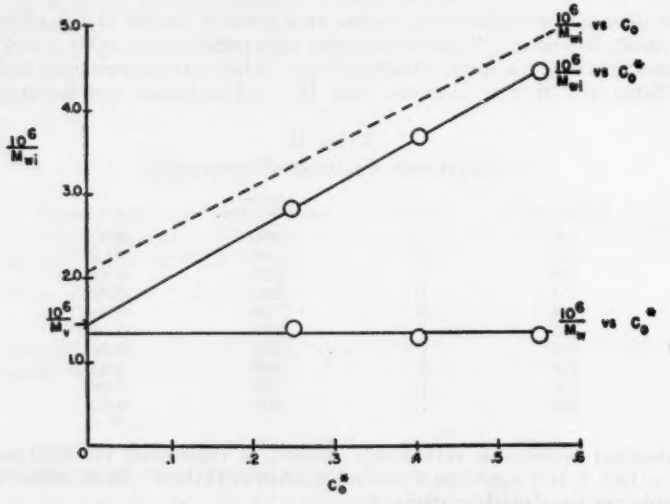


FIG. 2.—Effect of solute concentration on apparent weight-average molecular weight.

While the slope is about the same as given by the present method, the intercept is quite different. Evidence that the new method is superior is the fact that the viscosity-average molecular weight, M_v, is in good agreement with the present results, but not the former.

The results of the characterization of the polyisobutylenes are given in Table IV. Three average molecular weights, M_w, M_z, and M_{z+1} were cal-

TABLE IV

CHARACTERIZATION OF POLYISOBUTYLENES

Polymer	$M_w \times 10^{-5}$	$M_z \times 10^{-5}$	$M_{z+1} \times 10^{-5}$	Distribution[a,b]	M_n (calc.) $\times 10^{-5}$	M_v (calc.) $\times 10^{-5}$	$\eta_{1.2}$ (g./100 cc.)$^{-1}$	M_v (obs.) $\times 10^{-5}$	V
A	1.09	1.50	1.80	SCH $b=0.87$ $M_w=1.09\times10^5$	0.70	1.04	0.458	1.00	0.62
B	1.12	2.53	4.01	LK $\beta=1.18$ $M_0=0.40\times10^5$	0.58	1.00	0.477	1.01	1.12
E	7.50	12.4	18.0	LK $\beta=0.97$ $M_0=3.70\times10^5$	4.67	6.95	1.626	6.85	0.81
F	2.03	3.20	4.20	SCH $b=-0.23$ $M_w=2.05\times10^5$	0.89	1.87	0.696	1.93	0.76
H	8.31	17.8	24.0	Composite[c]	2.20	7.55	1.626	6.85	1.07
I	6.38	8.80	12.0	LK $\beta=0.79$ $M_0=4.05\times10^5$	4.74	6.06	1.533	6.28	0.62
K	5.09	6.75	8.20	SCH $b=1.18$ $M_w=5.10\times10^5$	3.50	4.94	1.326	5.05	0.57

[a] LK = Lansing-Kraemer distribution, see Equation (10).
[b] SCH = Schulz distribution, see Equation (11).
[c] Average of: LK $\beta=1.23$ SCH $b=-0.80$
$M_0=2.73\times10^5$ $M_w=9.0\times10^5$.

culated for each material studied. These three averages are then used to fit the molecular weight distribution to a parametric form. The two functions which were found effective in fitting the observed average molecular weights of these polyisobutylenes were the Lansing-Kraemer function[16]:

$$f(M)\,dM = \frac{1}{M_0\beta\sqrt{\pi}} \exp\left\{-\left(\frac{1}{\beta}\ln\frac{M}{M_0}\right)^2\right\} dM \qquad (10)$$

where:

$$\beta = \sqrt{2\ln(M_w/M_n)} = \sqrt{2\ln(M_z/M_w)} = \ldots\ 0 \leq \beta < \infty$$

and:

$$M_0 = M_w \exp\{-\tfrac{1}{4}\beta^2\}$$

and the Schulz function:

$$f(M)\,dM = \left(\frac{b+2}{M_w}\right)^{b+2} \cdot \frac{M^{b+1}}{\Gamma(b+2)} \exp\left\{-\left(\frac{b+2}{M_w}\right)M\right\} dM \qquad (11)$$

where:

$$b = (3M_w - 2M_z)/(M_z - M_w) \qquad -1 < b < \infty$$

In most cases good fits were obtained, that is, the assumed distribution accurately reproduced the observed average molecular weights. In the case of polymer H, it was necessary to use a composite function, an average of a Lansing-Kraemer and a Schulz function. The distribution functions are shown in Figures 3 and 4. It must be kept in mind that these are only approximate distributions, and cannot reproduce small details of the actual distribution.

If a parametric form of the molecular-weight distribution is known, it is a simple matter to calculate any average molecular weight. The number-average molecular weights (M_n) listed in Table IV were obtained in this way.

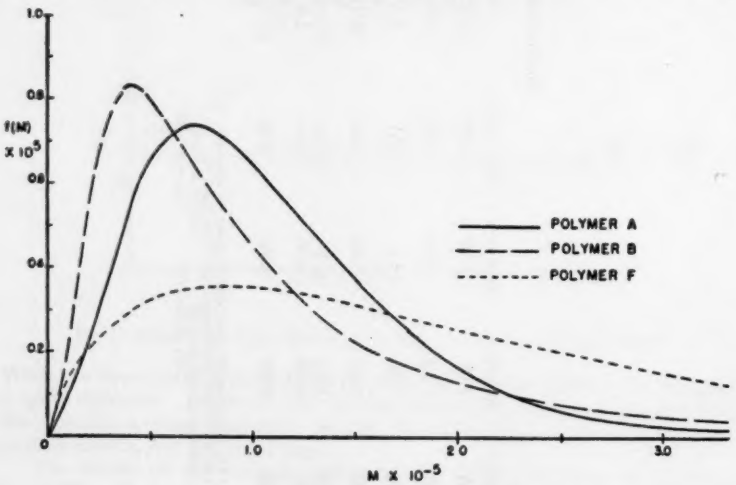


FIG. 3.—Molecular-weight distributions of polyisobutylenes.

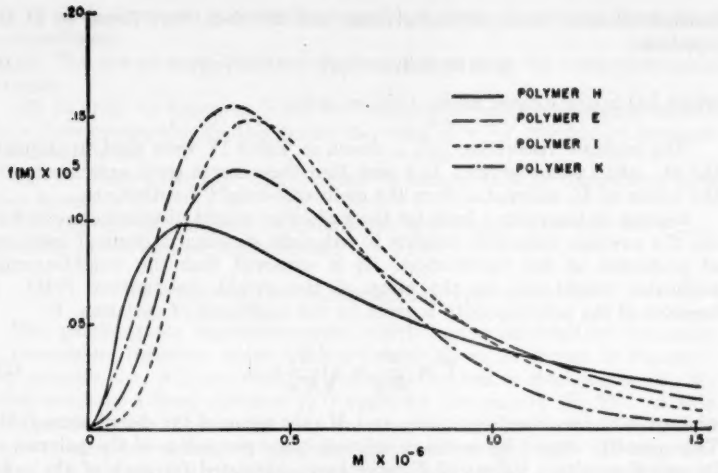


FIG. 4.—Molecular-weight distribution of polyisobutylenes.

In the case of polymer A it was found possible to calculate M_n directly from ultracentrifuge data, in the method suggested by Wales and coworkers[15]. The value obtained was 0.71×10^5, in excellent agreement with the value calculated from the molecular weight distribution, 0.70×10^5.

Another means of checking the molecular weight distributions is through intrinsic viscosity average molecular weights. This average is defined as:

$$M_v = [\int_0^\infty f(M)\, M^a\, dM]^{1/a} \tag{12}$$

where $f(M)$ is the normalized weight distribution, and a is the exponent in the empirical relation $[\eta] = KM^a$. It can easily be shown, by use of Equation (12) that the intrinsic viscosity-average molecular weights for a Lansing-Kraemer and for a Schulz distribution are:

$$\log \frac{M_v}{M_w} = \left(\frac{a-1}{2-2}\right) \log \frac{M_z}{M_w} \qquad \text{(Lansing-Kraemer)} \tag{13}$$

$$\log \frac{M_v}{M_w} = -\log (b+2) + \frac{1}{a} \log \frac{\Gamma(b+a+2)}{\Gamma(b+2)} \qquad \text{(Schulz)} \tag{14}$$

Values of M_v calculated in this way are listed in Table IV under the title M_v (calc.).

In order to obtain an independent check of the M_v values calculated, the intrinsic viscosities of the various polyisobutylenes were measured in toluene at $30.00 \pm 0.05°$ C. For this solvent and at this temperature, Fox and Flory[17] have shown that:

$$[\eta]_{1.2} = 2.0 \times 10^{-4} M_v^{0.67} \tag{15}$$

where $[\eta]_{1.2}$ is defined as the value of $(1/c) \ln (\eta/\eta_0)$ at $\eta/\eta_0 = 1.2$. The measurements were carried out in a Ubbelohde viscometer with a flow time for toluene at 30° C of about 275 seconds. The toluene used was redistilled from Baker's C.P. material. Flow times were measured for three or four

concentrations of each polyisobutylene, and the data were found to fit the equation:

$$(1/c) \ln (\eta/\eta_0) = [\eta] - 0.105\,[\eta]^2 c \tag{16}$$

where $[\eta]$ is now defined as $\lim_{c \to 0} (1/c) \ln (\eta/\eta_0)$.

The intrinsic viscosities, $[\eta]_{1,2}$, shown in Table IV were used to calculate the M_v (obs.) values given. It is seen that these are in good agreement with the values of M_v calculated from the molecular-weight distributions.

Instead of assuming a form for the molecular-weight distribution, one may use the average molecular weights to calculate standard statistical measures of properties of the distribution. It is apparent that the weight-average molecular weight will be the mean of the weight distribution, $f(M)$. A measure of the polydispersity is given by the coefficient of variation, V:

$$V = \frac{\sigma}{M_w} = \sqrt{\frac{M_z}{M_w}} - 1 \tag{17}$$

where σ is the standard deviation, and M_w the mean of the distribution $f(M)$. This quantity should be useful in relating other properties of the polymer to its polydispersity. Values of V have been calculated for each of the polyisobutylenes studied, and are given in Table IV.

VISCOELASTIC BEHAVIOR OF POLYISOBUTYLENES

We shall consider here the behavior of viscoelastic materials under constant shear stress. Following the notation of Alfrey[18], we may describe the response of a viscoelastic substance to a constant shear stress imposed at time $t = 0$ by the equation:

$$(\gamma/S) = J_0 + \int_0^\infty J(\tau)(1 - e^{-t/\tau})\, d\tau + t/\eta \tag{18}$$

Here, γ represents the shear strain and S the shear stress. The instantaneous elastic compliance is given by J_0. The second term describes the retarded elastic response; τ is the retardation time, and $J(\tau)$ the distribution of retardation times, that is, the compliance associated with retardation times between τ and $\tau + d\tau$. The quantity η is the viscosity associated with steady flow of the material.

If a material which obeys Equation (18) is subjected to a constant stress for a very long time, and that stress is then removed, elastic recovery will take place. If we now measure time from the moment at which the stress was removed, the recovery will be given by:

$$(\gamma/S) = \int_0^\infty J(\tau) e^{-t/\tau}\, d\tau + J_0 \tag{19}$$

The quantity:

$$\int_0^\infty J(\tau) d\tau = J_\infty \tag{20}$$

we shall call the steady state elastic compliance. Equations (18) and (19) describe what we shall call the creep and recovery curves, respectively, of a viscoelastic material. It is apparent that such curves, obtained from constant stress experiments, furnish a complete description of viscoelastic behavior at a given temperature.

While Equations (18) and (19) are very general in their applicability, emphasis should be made of several necessary restrictions and qualifications:

(*1*) Both stress and temperature must be maintained constant throughout an experiment.

(*2*) The sample must be free of residual stresses when the creep experiment is begun.

(*3*) In order for Equation (19) to be valid, the stress must have been applied for a time comparable to the maximum value of τ for which $J(\tau)$ becomes vanishingly small.

(*4*) In many cases the term J_0 may be insignificant in comparison with other terms.

(*5*) The viscosity η, and the compliance terms may vary with the stress, especially in the case of large stresses.

APPARATUS AND EXPERIMENTAL PROCEDURE

The parallel-plate viscoelastometer, which was constructed for the study of viscoelastic behavior under constant shear stress, is shown in Figure 5. The samples, (A, A′), are clamped between two heavy steel plates (B, B′) which are kept a fixed distance ($\frac{1}{2}$″) apart by the spacers (E, E′). A thin stainless steel plate (F) rests between the samples; to one end of this is attached a wire passing over a ball-bearing pulley (G) to the weight (H). To the other end of the thin plate is attached a small piece of glass (J) with a scale photographed upon it. A similar scale (K) is attached to the fixed part of the apparatus. The entire assembly is placed in an air thermostat which maintains a temperature constant to within $\pm 0.1°$ C.

The samples are disks of polyisobutylene, $\frac{1}{4}$ inch thick by 1 or $\frac{3}{4}$ inch in diameter. This thickness allows each sample to be compressed $\frac{1}{64}$ inch when the apparatus is clamped down, which should be sufficient to prevent slippage of these tacky materials. Samples are prepared in two ways. High molecular polyisobutylenes are formed in stainless steel molds, in a hydraulic press, at 60–70° C. The lower molecular materials, which would adhere to the molds, are cast in tinfoil cups at the same temperature. The tinfoil is removed by amalgamation with mercury. In both procedures sufficient time is allowed for residual stresses to relax.

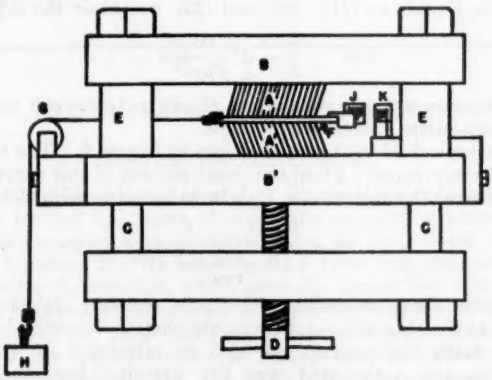


FIG. 5.—Viscoelastometer.

The samples, with the thin plate between them, are then placed in the apparatus, and carefully aligned with the aid of machined blocks and pins. After a period for relaxation of residual stress induced by this process, the alignment blocks and pins are removed, and the samples again allowed to rest, for a somewhat shorter period.

The weight is then attached, and the experiment begun. The weight exerts a shearing stress on the samples, which produces a shear strain, with a resulting horizontal displacement of the thin metal plate. This displacement is measured by photographing, through a simple optical system, the two pieces of scale. The distance between a pair of lines is measured with a Gaertner microcomparator, with a precision of ± 0.0002 cm.

CALCULATIONS

The calculation of absolute shear strain and stress for these experiments is much facilitated by the simple geometry of the instrument. If the deflection of the moving scale relative to the reference position (measured on the photographic plate) is Δ', the reciprocal magnification factor of the optical system is f, and the thickness of each sample is h, then the shear strain is given by:

$$\gamma = \Delta' f/h \tag{21}$$

Furthermore, if the force exerted by the weight (neglecting any small friction in the pulley) is F, and the average horizontal cross-sectional area of each sample is A, the stress is:

$$S = F/2A \tag{22}$$

The cross-sectional area is calculated by the relation:

$$2A = (V/h) = W/\rho_T h \tag{23}$$

where V = the total volume of the two samples, W = the total weight of the two samples, and ρ_T is the density of polyisobutylene at the temperature of the experiment. The density data were obtained from Ferry[19]. The factor f was determined by measuring a known distance on the scale in the photographs, and was found to be 0.954 ± 0.002.

Combining Equations (21), (22), and (23), we obtain the expression:

$$\frac{\gamma}{S} = \Delta' \frac{fW}{F\rho_T h^2} \tag{24}$$

This is the fundamental equation which allows us to convert the observed Δ' values to strain/stress values in c.g.s. units.

Part of a typical Δ' vs. t plot is shown in Figure 6. The upper curve is the observed creep curve. From the linear portion of this curve at very long times (not shown) the viscosity, η, may be calculated, using the relation:

$$\eta = \frac{F\rho_T h^2}{fW} \frac{1}{\lim\limits_{t\to\infty} (d\Delta'/dt)} \tag{25}$$

The lower solid curve represents the elastic recovery, calculated from the deformation at the time the weight was removed, and considering this as zero time. The elastic deformation can also be calculated by subtracting the viscous deformation (calculated from the viscosity) from the creep curve. This is shown as the broken line in Figure 6. This procedure becomes unreliable at long times, since it then involves taking the difference between two

very large numbers, the total deformation and the viscous deformation. Since the elastic recovery approaches a limiting value at very long times, it is possible to obtain an independent check of the viscosity by subtracting this steady-state elastic deformation from the total deformation at the end of the creep experiment. The deformation thus obtained can be considered to be entirely due to flow of the material.

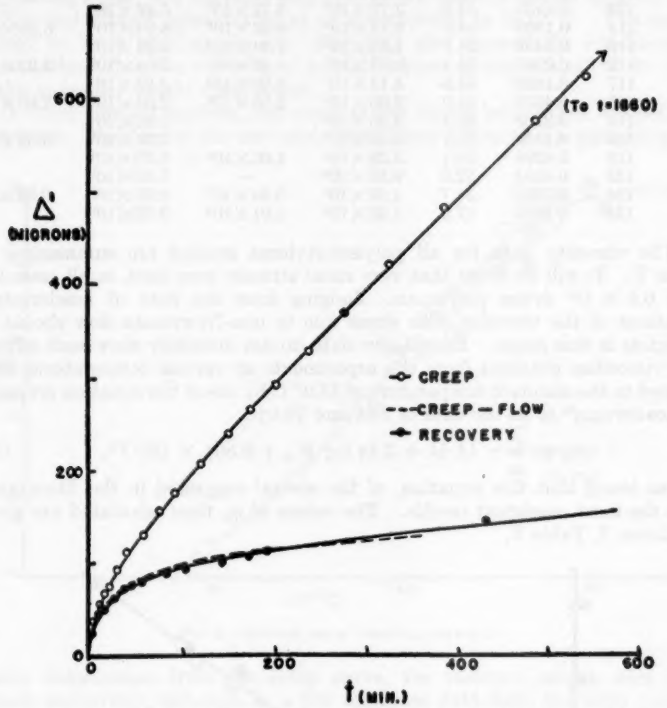


FIG. 6.—Creep and recovery, polymer 1, Experiment 113.

RESULTS AND CONCLUSIONS

The viscoelastic behavior of several of the previously described polyisobutylenes was studied by means of creep and recovery experiments. The viscosities of the samples were calculated from the final slopes of the creep curves, using Equation 25. In most cases, a value was also obtained from the nonrecoverable deformation, which generally agreed well with the former value. In one instance (Experiment 116), there is a considerable discrepancy; here, the value from the creep curve was accepted as more reliable, since the extrapolation of the recovery curve to infinite time is somewhat doubtful. In a few cases (Experiments 114, 115, 123) temperature changes during the early part of the creep experiment make viscosities calculated from nonrecoverable deformation unreliable.

TABLE V

VISCOSITIES OF POLYISOBUTYLENES

Polymer	Expt.	S (dynes/cm.^{2} × 10^{-4})	T (° C.)	η_T (creep)	η_T (non-rec.) (poises)	η_{35} (calc.)	η_{35} (av.)
A	110	0.0749	35.3	3.89×10^6	4.14×10^6	4.09×10^6	3.97×10^6
	118	0.0786	15.7	2.18×10^7	2.06×10^7	3.84×10^6	
	122	0.4137	35.6	3.77×10^6	3.72×10^6	3.86×10^6	
B	111	0.1599	35.3	6.19×10^6	6.02×10^6	6.24×10^6	6.24×10^6
	119	0.3495	24.7	1.54×10^7	1.44×10^7	6.21×10^6	
F	112	0.0963	35.1	3.75×10^7	3.88×10^7	3.86×10^7	3.92×10^7
	117	0.1930	34.8	4.13×10^7	4.00×10^7	3.98×10^7	
I	113	0.4553	35.0	2.00×10^9	2.06×10^9	2.03×10^9	2.03×10^9
	114	0.2269	63.4	2.85×10^8	—	1.96×10^9	
H	115	0.4345	45.7	1.45×10^9	—	3.23×10^9	3.30×10^9
	116	0.4298	35.1	3.28×10^9	4.00×10^9	3.30×10^9	
	123	0.4391	52.5	9.86×10^8	—	3.53×10^9	
K	124	0.2269	34.7	1.00×10^9	0.94×10^9	0.95×10^9	0.95×10^9
	125	0.2197	67.0	1.02×10^8	1.01×10^8	0.92×10^9	

The viscosity data for all polyisobutylenes studied are summarized in Table V. It will be noted that very small stresses were used, in all cases less than 0.5×10^4 dynes per sq.cm. Judging from the data of Leaderman[20], variations of the viscosity with stress due to non-Newtonian flow should be negligible in this range. Indeed, our data do not definitely show such effects. The viscosities obtained from the experiments at various temperatures were reduced to the standard temperature of 35.0° C by use of the equation proposed by Leaderman[20] to fit the data of Fox and Flory;

$$\log \eta_T = -14.44 + 3.14 \log M_w + 0.504 \times 10^6/T^2 \qquad (26)$$

It was found that this equation, of the several suggested in the literature[21], gave the most consistent results. The values of η_{35} thus calculated are given in column 7, Table V.

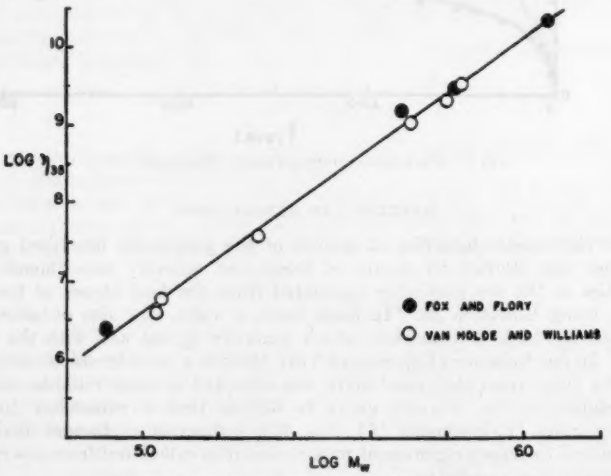


FIG. 7.—Log η vs. log M_w polyisobutylene at 35.0° C.

Since there appears to be some slight disagreement among the published results of the temperature dependence of the viscosity of polyisobutylene, average viscosities at 35.0° C were calculated from experiments performed within a few tenths of a degree of this temperature. These are listed in the last column of Table V. In Figure 7, the logarithms of these viscosities are plotted vs. the logarithms of the weight-average molecular weights of the polyisobutylenes. On the same graph are shown viscosity values from the data of Fox and Flory[22], interpolated at or extrapolated to 35.0° C. The results appear to be in good agreement. Our data also support the conclusion of these authors that the viscosity of polyisobutylene is independent of the form of the molecular weight distribution.

A more detailed analysis was made of the elastic behavior of the polyisobutylenes. Because of the previously mentioned difficulties in separating the

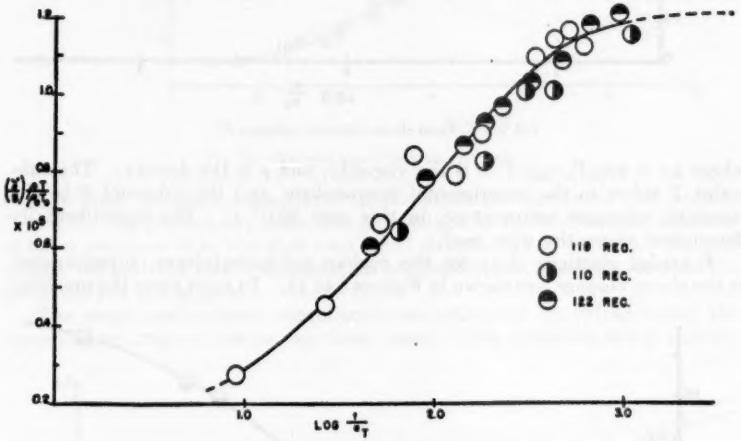


FIG. 8.—Reduced elastic behavior, polymer A.

elastic deformation from the creep curve, the recovery curves were used almost exclusively, although in a few instances data from the early part of the creep experiments were recorded. In favorable cases (high viscosity) the agreement between elastic behavior calculated from creep and recovery experiments was quite satisfactory.

Since the retarded elastic recovery usually took place over several decades of logarithmic time, it was advantageous to perform experiments on each sample at two or more temperatures. These results were then reduced to the standard temperature of 35.0° C by the method of semireduced variables, developed by Ferry[23]. This method, which has been used with considerable success by Ferry and coworkers[3] in studying dynamic-mechanical properties, and by Tobolsky and coworkers[24] with stress relaxation data, was found to be extremely useful. According to this procedure, results obtained at different temperatures may be superimposed by plotting:

$$\frac{\gamma}{S}\frac{\rho T}{\rho_0 T_0} \text{ vs. } \log \frac{t}{a_T}$$

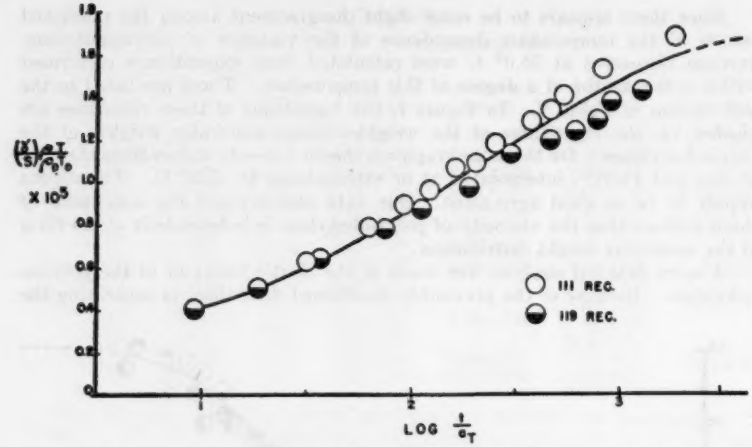


FIG. 9.—Reduced elastic behavior, polymer B.

where $a_T = \eta_T \rho_0 T_0 / \eta_0 \rho_T T$, η is the viscosity, and ρ is the density. The subscript T refers to the experimental temperature, and the subscript 0 to the standard reference temperature, in this case 35.0° C. The experimentally determined viscosities were used.

Retarded elasticity data for the various polyisobutylenes, superimposed in the above manner, are shown in Figures 8 to 13. In most cases the precision

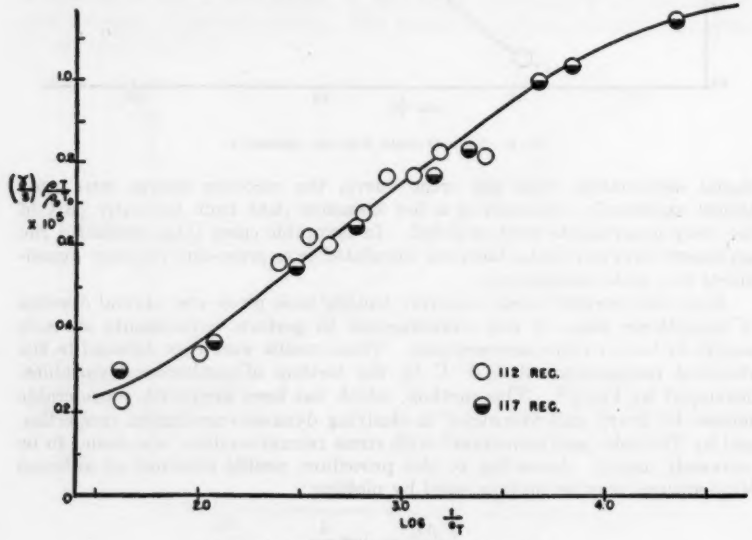


FIG. 10.—Reduced elastic behavior, polymer F.

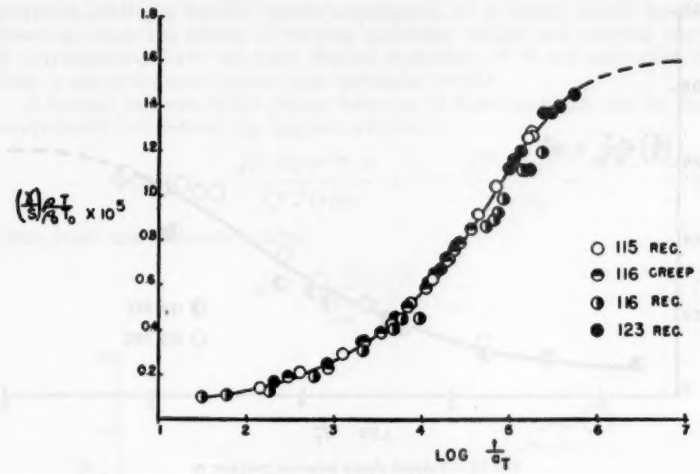


FIG. 11.—Reduced elastic behavior, polymer H.

is quite good, although some scatter is evident in the results for polymers A, B, and K. In the first two cases, this is explained by the fact that the viscosity of these polymers is so low that very small stresses had to be used. This, of course, reduced the elastic deformation and subsequent recovery, so that the precision was not as good.

The steady-state elastic compliance was estimated by extrapolating the sigmoidal recovery curves to very long times. This procedure is not entirely

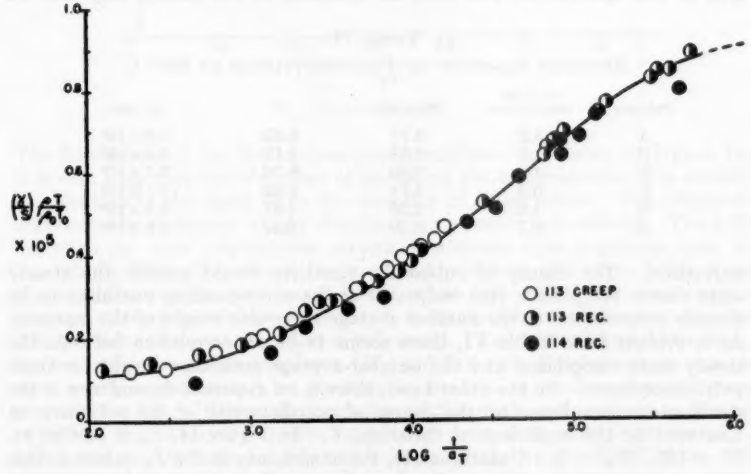


FIG. 12.—Reduced elastic behavior, polymer I.

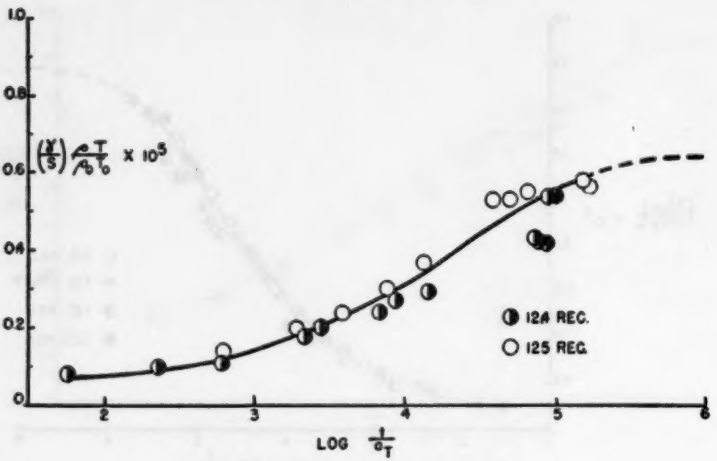


FIG. 13.—Reduced elastic behavior, polymer K.

satisfactory, since insufficiently long creep and recovery experiments make the extrapolation relatively arbitrary. Thus the values of J_e, the steady state elastic compliance, given in Table VI, cannot be said to be accurate to more than 10 per cent.

There exists at the present time no completely satisfactory theory of elastic behavior of linear high polymers. It has been proposed[18] that the theory of rubberlike elasticity, as developed for cross-linked polymers, should be applicable to linear polymers as well, but there has been no experimental verification of this speculation, and such an extension of the theory may well be

TABLE VI

RETARDED ELASTICITY OF POLYISOBUTYLENES AT 35.0° C

Polymer	$J_e \times 10^5$ (cm.^{3}/dyne)	$M_n \times 10^{-4}$	V	$\bar{\tau}_{35}$ (sec.)
A	1.2	0.71	0.62	1.5×10^2
B	1.7	0.58	1.12	4.4×10^2
F	1.2	0.89	0.76	3.7×10^3
I	0.9	4.74	0.62	1.1×10^5
H	1.6	2.20	1.07	3.3×10^5
K	0.7	3.50	0.57	4.6×10^4

unjustified. The theory of rubberlike elasticity would predict the steady state elastic compliance (the reciprocal of the corresponding modulus) to be directly proportional to the number average molecular weight of the material. As is evident from Table VI, there seems to be no correlation between the steady state compliance and the number-average molecular weight for these polyisobutylenes. On the other hand, there is an apparent dependence of the steady-state compliance on the degree of polydispersity of the polymers, as measured by the coefficient of variation, V. In Figure 14, J_e is plotted *vs.* $V^2 = (M_z/M_w) - 1$. Unfortunately, the uncertainty in the J_e values forbids us to make more than the qualitative assertion that the more homogeneous

polymers exhibit a smaller elastic compliance, or a higher elastic modulus. However, since the effects of varying molecular weight and varying degrees of polydispersity have not been studied separately, it is not impossible that there is also some dependence upon molecular weight.

A further analysis of the elastic behavior of these materials can be made. Leaderman[20] has defined the function $\psi(t)$ as:

$$\psi(t) = 1 - \frac{\int_0^\infty J(\tau)e^{-t/\tau}\,d\tau}{\int_0^\infty J(\tau)d\tau} = 1 - \frac{\int_0^\infty J(\tau)e^{-t/\tau}\,d\tau}{J_\infty} \tag{27}$$

Thus, from elastic recovery data:

$$\psi(t) = \frac{(\gamma(t)/S)_{rec.}}{\lim_{t\to\infty}(\gamma(t)/S)_{rec.}} \tag{28}$$

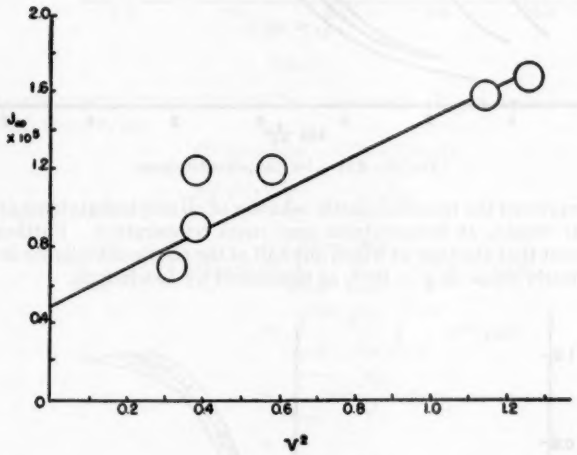


FIG. 14.—J_∞ *vs.* V^2.

The functions $\psi(t)$ for the various polyisobutylenes are shown in Figure 15. It is seen from this that the effect of increasing the molecular weight is to shift the function to the right, or in the direction of longer times. The effects of differences in molecular weight distribution are small but definite. The $\psi(t)$ functions for very polydisperse materials extended over a greater span of logarithmic time than those for more homogeneous polymers. One may compare, for example, polymers A and B, which have nearly the same weight-average molecular weight. Polymer B is much more polydisperse and its $\psi(t)$ function is broader than that of polymer A. Leaderman[20] has shown that, for low-molecular polyisobutylenes ($M_w < 0.7 \times 10^5$), the $\psi(t)$ curves can be very nearly superimposed by plotting *vs.* $\log t/\eta$. A similar plot has been prepared for the polyisobutylenes studied in this work, and is shown in Figure 16. Here $\psi(t)$ is plotted against $\log t \times 10^5/a_T\eta_{35}$, and, aside from the small differences attributable to differences in molecular-weight distribution, the curves very nearly superimpose. Thus, a single curve may be said to approxi-

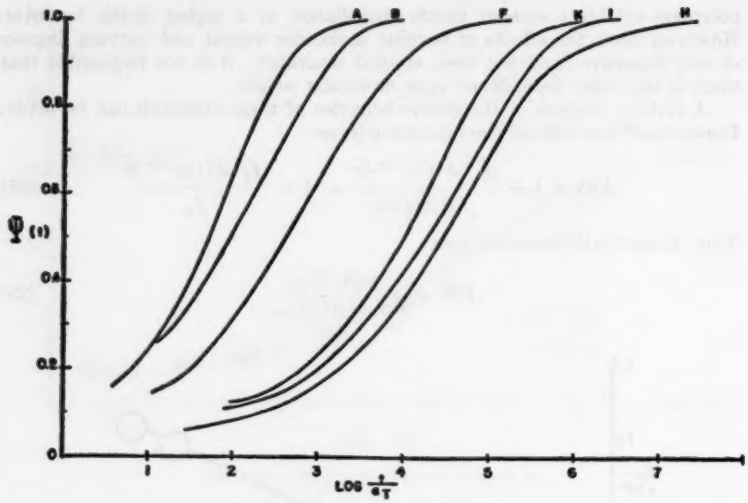


FIG. 15.—$\Psi(t)$ *vs.* log t/a_T polyisobutylenes.

mately represent the retarded elastic behavior of all polyisobutylenes of medium molecular weight, at temperatures near room temperature. Furthermore, it is of interest that the time at which one half of the elastic compliance is manifest is very nearly equal to $\eta \times 10^{-5}$, as mentioned by Leaderman.

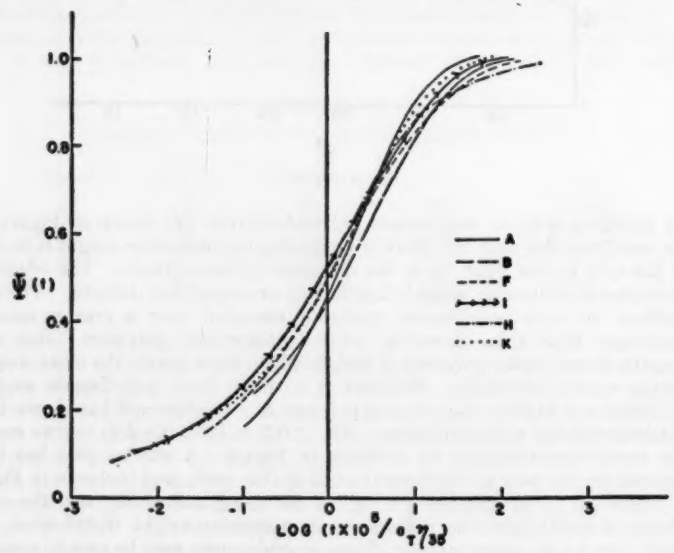


FIG. 16.—Superimposed $\Psi(t)$ curves.

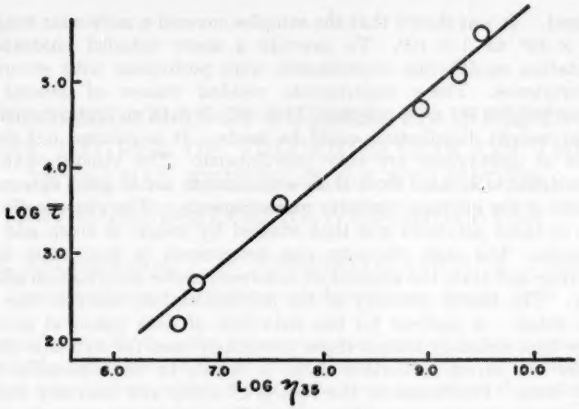


FIG. 17.

One more point of interest should be mentioned. If one defines an average retardation time, $\bar{\tau}$, as:

$$\bar{\tau} = \frac{\int_0^\infty \tau J(\tau)\, d\tau}{\int_0^\infty J(\tau)\, d\tau} = \frac{\int_0^\infty \tau J(\tau)\, d\tau}{J_\infty} \tag{29}$$

It is apparent that:

$$\begin{aligned}\int_{t=0}^{t=\infty} [1 - \psi(t)]\, dt &= \int_{t=0}^{t=\infty} \int_{\tau=0}^{\tau=\infty} \frac{J(\tau)}{J_\infty} e^{-t/\tau}\, d\tau dt \\ &= \int_{\tau=0}^{\tau=\infty} \frac{J(\tau)}{J_\infty} \int_{t=0}^{t=\infty} e^{-t/\tau}\, dt d\tau \\ &= \int_{\tau=0}^{\tau=\infty} \tau \frac{J(\tau)}{J_\infty} d\tau \\ &= \bar{\tau}\end{aligned} \tag{30}$$

Thus, integration of the function $1 - \psi(t)$ will yield the average retardation time. This integration was carried out by plotting $\psi(t)$ *vs.* t, in segments, and measuring the area between this curve and the $\psi = 1$ ordinate with the aid of a planimeter. The values of $\bar{\tau}$ thus obtained are listed in the last column of Table VI. In Figure 17, the logarithms of these average retardation times are plotted *vs.* the logarithm of the viscosity at 35.0° C. The straight line which is passed through these points has a slope of 1.00. Thus, the average retardation time is directly proportional to the viscosity of the polyisobutylene. The data may be fit quite well by the expression:

$$\bar{\tau}_{35} = 8.0 \times 10^{-5}\, \eta_{35} \tag{31}$$

SYNOPSIS

A study was made of the behavior under constant shear stress of several carefully characterized samples of polyisobutylene. The materials used were whole polymers and fractions obtained from these by fractional precipitation. As a first step in the characterization, the intrinsic viscosity of each was

determined. It was shown that the samples covered a molecular weight range from 1×10^5 to 1×10^6. To provide a more detailed characterization, sedimentation equilibrium experiments were performed with several of the polyisobutylenes. These experiments yielded values of several average molecular weights for each polymer, from which data an approximation to the molecular weight distribution could be made. It is pointed out that whole polymers of isobutylene are very polydisperse. The viscosity-average molecular weights calculated from these experiments are in good agreement with the results of the intrinsic viscosity measurements. The viscoelastic behavior of some of these polymers was then studied by means of creep and recovery experiments. The melt viscosity was determined in two ways, from flow during creep and from the amount of non-recoverable deformation after elastic recovery. The elastic recovery of the polyisobutylene samples was analyzed in some detail. A method for the reduction of data taken at several temperatures to a standard temperature, previously used for dynamic-mechanical properties and stress relaxation data, is shown to be applicable to elastic recovery data. Furthermore, the results of creep and recovery experiments can be superimposed in favorable cases. The steady-state elastic compliance is evaluated, and errors in its determination are discussed. The results seem to indicate that this quantity depends, at least in part, on the degree of polydispersity of the polymer. This dependence appears to mask any direct variation with average molecular weight. Finally, it is shown that an average retardation time is directly proportional to the melt viscosity of the polymer.

ACKNOWLEDGMENT

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REFERENCES

[1] Fox and Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948); *J. Phys. & Colloid Chem.* **55**, 221 (1951).
[2] Andrews, Hofman-Bang, and Tobolsky, *J. Polymer Sci.* **3**, 669 (1948); Andrews and Tobolsky, *J. Polymer Sci.* **7**, 221 (1951); Tobolsky and McLoughlin, *J. Polymer Sci.* **7**, 543 (1952).
[3] Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950); Ferry, Fitzgerald, Johnson, and Grandine, *J. Applied Physics* **22**, 717 (1951).
[4] These polymers were obtained from the Esso Laboratories, Standard Oil Development Co., Linden, N. J.
[5] Fox and Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948).
[6] Svedberg, and Pederson, "The Ultracentrifuge," Oxford University Press, London, **1940**.
[7] Wales, *J. Phys. & Colloid Chem.* **53**, 197 (1949); **55**, 282 (1951); Wales, Adler, and Van Holde, *J. Phys. & Colloid Chem.* **55**, 145 (1951).
[8] This was 99.5(+)% octane of Eastman Kodak.
[9] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, Vol. 1, **1939**.
[10] Gosting and Morris, *J. Am. Chem. Soc.* **71**, 1998 (1949).
[11] Wales, *J. Phys. & Colloid Chem.* **53**, 197 (1949).
[12] Wales, *J. Phys. & Colloid Chem.* **53**, 197 (1949); Goldberg, *J. Phys. Chem.* **57**, 194 (1953).
[13] Wales, *J. Phys. & Colloid Chem.* **55**, 282 (1951).
[14] Wales, Adler, and Van Holde, *J. Phys. & Colloid Chem.* **55**, 145 (1951); Some recent and not yet published results by P. Flory have been called to our attention since this paper was prepared. An osmotic pressure study shows that B varies slightly with the molecular weight of polyisobutylene in cyclohexane. Such a variation in isooctane, which may be indicated by the above data, would produce errors for very high or very low molecular weights, since we have used an average value of B. We feel that in the molecular weight range which we have studied, such errors should be small. It should be pointed out that the theory of sedimentation equilibrium, as applied here, implicitly assumes the virial coefficient to be negligibly small.
[15] Wales, Adler, and Van Holde, *J. Phys. & Colloid Chem.* **55**, 145 (1951).
[16] Lansing and Kraemer, *J. Am. Chem. Soc.* **57**, 1369 (1935).
[17] Fox and Flory, *J. Phys. & Colloid Chem.* **53**, 197 (1949).
[18] Alfrey, "The Mechanical Behavior of High Polymers," Interscience Publishers, Inc., New York, **1948**.
[19] Ferry, J. D., private communication.
[20] Leaderman, Smith, and Jones, "The Rheology of Polyisobutylene," National Bureau of Standards Report; Technical Report No. 7 to the Office of Naval Research, **1951**.
[21] Fox and Flory, *J. Phys. & Colloid Chem.* **55**, 221 (1951); Andrews and Tobolsky, *J. Polymer Sci.* **7**, 221 (1951); Leaderman, Smith, and Jones, "The Rheology of Polyisobutylene," National Bureau of Standards Report; Technical Report No. 7 to the Office of Naval Research, **1951**.
[22] Fox and Flory, *J. Phys. & Colloid Chem.* **55**, 221 (1951).
[23] Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).
[24] Andrews and Tobolsky, *J. Polymer Sci.* **7**, 221 (1951); Tobolsky and McLoughlin, *J. Polymer Sci.* **7**, 543 (1952).

THE VULCANIZATION OF RUBBER. XI. INFLUENCE OF THE DEGREE OF VULCANIZATION ON THE INTERNAL FRICTION OF UNLOADED BUTADIENE-STYRENE VULCANIZATES *

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It is well known that, in the vulcanization of rubber in the range as far as ebonite, all the properties of the polymer change sharply. In particular, the vitrification temperature, which is one of the most important characteristics of relaxation, changes considerably[1]. On the other hand, as was recently shown by the authors[2], for soft vulcanizates which contain up to 3 per cent of total sulfur, the relaxation properties, and consequently also the internal friction, which is responsible for heat build-up during dynamic deformation, are independent of the period of vulcanization. The independence of internal friction from the degree of vulcanization of soft vulcanizates can be explained in that case by assuming that the presence of the spatial network of the vulcanizate does not influence the heat motion of the segments between the cross-links as long as the cross-links of this network are distributed sufficiently far apart.

Hence it is of particular interest to explain what average distance between the cross-links of the spatial network of the vulcanizate is critical with respect to its influence on the heat motion of the segments of the polymeric chains between the cross-links and on the internal friction of the rubber. The principal characteristics manifest in the mechanical behavior of vulcanizates with high sulfur contents are interesting from a practical viewpoint, for they indicate the limits with which it is possible, by means of vulcanization, to change the hardness of rubber without danger of thereby increasing its internal friction.

The purpose of this work is to study the problem of the influence of side-chain development of the spatial structure, determined by the number of transverse cross-bonds which are formed during the vulcanization process, on the internal friction which occurs in the reversible deformation of vulcanizates.

METHODS AND OBJECTS OF STUDY

Unloaded vulcanizates of butadiene-styrene rubber with various concentrations of combined sulfur served as test-specimens. The selection of butadiene-styrene rubber was governed by the desirability of avoiding the complicating influence of crystallization. Besides, experimental studies of the thermodynamics of deformation of vulcanizates, made in recent years by Bartenev[3], showed that the elastic properties of vulcanizates of butadiene-styrene rubber approach the properties of an ideal rubber.

The vulcanizates were prepared as films 1 mm. thick. For testing the rebound resilience according to Kornfeld, special discs 6 mm. thick were prepared. Ten different vulcanizates, differing in sulfur content and vulcanization

* Translated for Rubber Chemistry & Technology from the *Kolloidnyi Zhurnal*, Vol. 14, No. 6, pages 444–455 (1952).

time, were studied. For all the vulcanizates, the content of total and free sulfur was determined analytically. The combined sulfur content was calculated from the difference between the total and free sulfur (see Table 1).

In this method it is clearly necessary to take into account that, in the different samples, the free sulfur contents are not the same. However, we shall assume that chemically uncombined sulfur in the quantities in which it was found

TABLE 1

ANALYSIS OF VULCANIZATES CONTAINING DIFFERENT PROPORTIONS OF TOTAL SULFUR

No.	Sulfur added (%)	Vulcanization time in press at 143° C (min.)	Sulfur determined by analysis (%)		
			Total	Free	Combined
1	0.96	40	0.66	0.25	0.41
2	1.44	40	1.51	0.23	1.28
3	2.83	40	3.24	0.51	2.73
4	4.63	40	4.96	0.67	4.29
5	6.35	40	6.90	1.30	5.60
6	8.85	60	9.54	2.10	7.44
7	12.7	60	13.70	4.81	8.89
8	17.6	120	19.95	9.93	10.02
9	23.7	180	26.40	12.20	14.20
10	32.6	270	38.20	11.65	26.55

in the samples studied, has little effect on internal friction, and the differences of the corresponding indexes for the samples are caused only by the differing contents of chemically combined sulfur. The basis for such an assumption is particularly the fact that the last two vulcanizates (Table 1), which differ especially in internal friction (see Table 2 below), contain practically equal proportions of free sulfur.

MEASUREMENT OF INTERNAL FRICTION OF RUBBERS

For measuring internal friction, which is responsible for heat formation during dynamic deformation, besides special tests on a Bidermann pendulum apparatus, the widely used method of measuring rebound resilience on a Schob apparatus and dynamic hysteresis during forced vibrations on a Kornfeld vibrator[4] were employed. As an arbitrary index of the internal friction of rubber (for a given frequency of deformation) was taken a value equal or proportional to the amount of heat formed in a unit volume of material for one cycle in the dynamic system established by a constant amplitude of deformation. In the experiments with the Kornfeld apparatus, the values measured represent the dynamic modulus of compression E and the sine of the angle of mechanical loss sine φ.

It is easy to show that the value, which is approximately proportional to the internal friction, at the given frequency, of the material studied, is the product of $\pi \cdot E \cdot \tan \varphi$.

The latter follows directly from the equation:

$$\tan \varphi = \frac{\omega \eta}{E} \qquad (1)$$

which, in turn, follows from the hypothesis that the forced oscillations of the rubber test-specimen (if its mass in comparison with the mass of the moving

TABLE 2

INDEXES OF INTERNAL FRICTION AND EQUILIBRIUM MODULI OF VULCANIZATES CONTAINING VARIOUS PERCENTAGES OF COMBINED SULFUR

Combined sulfur (%)	$\pi E \tan \varphi$ (ergs per cc. $\times 10$) (Kornfeld machine)	$\frac{E(1-R)}{2}$ (ergs per cc. $\times 10^7$) (Schob machine)	$\frac{\Delta W}{V\theta}$ in ergs per cc. $\times 10^6$ (pendulum machine of SRIRI)								E_∞ (dynes/sq. cm. $\times 10^6$ at 70° C)
			Effective mass 500 g.				Effective mass 250 g.				
			$\epsilon_0=0$ $\varphi_0=90°$	$\epsilon_0=0$ $\varphi_0=120°$	$\epsilon_0=0.05$ $\varphi_0=90°$	$\epsilon_0=0.5$ $\varphi_0=120°$	$\epsilon_0=0$ $\varphi_0=90°$	$\epsilon_0=0$ $\varphi_0=120°$	$\epsilon_0=0.5$ $\varphi_0=90°$	$\epsilon_0=0.5$ $\varphi_0=120°$	
0.40	1.36	0.78	2.61	2.12	1.70	1.60	2.88	2.30	1.63	1.53	0.61
1.28	1.45	0.75	2.36	1.98	1.67	1.57	2.53	2.13	1.62	1.52	2.45
2.73	1.48	0.71	2.01	1.75	1.66	1.64	2.13	1.95	1.59	1.62	9.48
4.29	1.41	0.77	1.86	1.62	1.72	1.53	1.95	1.72	1.60	1.60	10.8
5.60	1.30	0.81	1.73	1.44	1.64	1.39	1.79	1.48	1.55	1.27	12.4
7.44	1.50	0.80	1.91	1.63	1.62	1.59	2.00	1.67	1.61	1.63	13.1
8.89	1.49	0.78	2.10	1.63	1.81	1.69	2.21	1.68	1.72	1.65	13.6
10.02	1.40	1.06	2.21	1.82	2.01	1.71	2.41	1.93	1.98	1.77	20.1
14.20	2.44	2.56	21.05	14.80	17.20	15.11	23.55	16.10	18.21	14.99	46.5
26.55	—	—	348.0	150.0			329.0	143.0			68.0

parts of the apparatus is ignored) can be described, as a first approximation, by the differential equation:

$$f \cos \omega t = E_{\epsilon} + \eta \frac{d\epsilon}{dt} \tag{2}$$

where ϵ is the deformation; f is the magnitude of the deforming force; ω is the frequency of oscillation; t is the time, and η is the internal friction of the rubber.

The product of $\pi \cdot E \tan \varphi = \pi\omega\eta$ expresses, as a first approximation, the work converted into heat for one cycle of oscillation for the given amplitude of deformation which is equal to unity.

In the tests with the Schob pendulum apparatus, the index is the so-called elasticity R, which represents the ratio of the useful work to the total work of one deformation cycle. The basic defect of the Schob apparatus consists in the fact that the dynamic deformation which the test-specimen undergoes under the impact of the pendulum hammer is not measured, and is not considered. Hence any evaluation of the internal friction from the data on the rebound resilience, measured on the Schob apparatus, is impossible at this time.

However, using the value of the dynamic modulus of compression E, obtained with the same specimens on the Kornfeld apparatus, the coefficient of internal friction can be calculated from the approximate formula[5]:

$$K_{y \cdot 0} = \pi\eta\omega \approx \frac{E(1 - R)}{2} \tag{3}$$

which is accurate for small values of $\frac{\eta\omega}{E}$.

In Equation (3), $K_{y \cdot 0}$ is the coefficient of internal friction, measured by the rebound resilience $(y \cdot 0)$ and R is the index of elasticity.

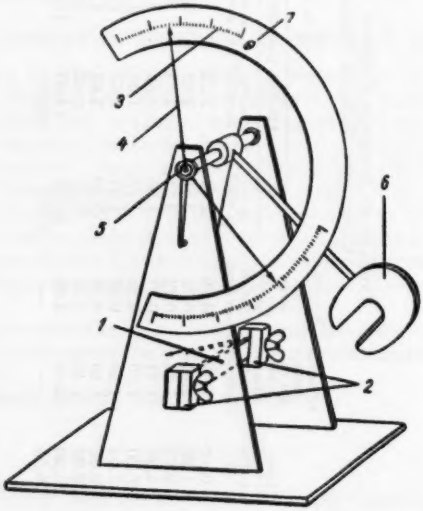

FIG. 1.—Biderman pendulum apparatus.

The most reliable measurements of the index of internal friction of the vulcanizates studied were obtained with the pendulum apparatus which is shown schematically in Figure 1. Inasmuch as in the apparatus indicated, rebound resilience played a part, it was advisable to study the principal characteristics which determine the advantages of the pendulum apparatus over the Schob apparatus.

These characteristics are:

(1) The deformation which the test-specimen undergoes from the pendulum hammer is a uniaxial strain. This situation is assured by the fact that the specimen tested is not a disc, but a rubber strip, 1, fastened between two clamps, 2, and set perpendicular to the plane of oscillation of the pendulum hammer.

(2) In every experiment, not only the angle of rebound of the pendulum after striking the specimen is measured, but also the deformation of the specimen from the blow. The deformation is measured on a special scale, 3, by means of a pointer, 4, which can turn with light friction relative to the axis, 5, of the oscillating system. Because of the presence of a special stop, 7, which blocks the movement of the pointer from the moment the hammer comes into contact with the specimen, the pointer is forced to turn with respect to the oscillating system. This continues until the hammer stops, before reversing itself, and the corresponding angle, recorded on the scale, 3, indicates the maximum deformation of the test-specimen from the blow.

(3) The construction of the apparatus makes possible moving the specimen in the clamps in the undeformed state, as well as when deformed to the desired degree; this makes it possible to study the effect of a preliminary stretching on the hysteresis of the particular vulcanizate.

(4) The apparatus has an additional hammer with removable weights, which permit the testing of materials of different modulus under conditions of constant dynamic deformation.

In each experiment, the following indexes were measured and calculated: a, the width of the strip tested; δ its area; V the volume of the dynamic section.

When the specimen is fastened between the clamps in the deformed state, then:

$$V = V_0 \frac{1}{\lambda_0} = a\delta L_0 \frac{1}{\lambda_0} \tag{4}$$

where L_0 is the distance between the clamps of the apparatus, λ_0 is its relative length. Further we have: φ_0, the angle of the height of fall of the pendulum hammer; φ_1, the angle of the rebound of the pendulum hammer after it strikes the specimen; φ_2, the angle of maximum deformation of the specimen from the blow; d, the maximum displacement of the center of the deformed specimen from the flow:

$$d = 2r \sin \frac{\varphi_2}{2} \tag{5}$$

where r is the distance from the center of oscillation of the pendulum to the center of the test-specimen.

For the apparent dynamic deformation, we take:

$$\epsilon_1 = \frac{L}{L_0} - 1 = \sqrt{\frac{4d^2}{L_0^2} + 1} - 1 \tag{6}$$

where L is the length of the dynamic segment in the test-specimen deformed by the action of the hammer.

It is possible to show that the following relation exists between the apparent dynamic deformation and the complete deformation:

$$\epsilon = \epsilon_1 + \epsilon_1\epsilon_0 + \epsilon_0 \tag{7}$$

Evidently in the particular case of the absence of static deformation ($\epsilon_0 = 0$), the total deformation is equal to the dynamic deformation $\epsilon = \epsilon_1$.

Equation (7) is obtained thus. We have:

$$\epsilon_0 = \frac{L_0}{L_{(\epsilon_0=1)}} - 1 \tag{8}$$

here $L(\epsilon_0 = 1)$ represents the length of the dynamic section of the test-specimen (corresponding to the distance between the clamps of the apparatus) in the undeformed state. From Equation (8) it follows that:

$$L_{(\epsilon_0=0)} = \frac{L_0}{\epsilon_0 + 1} \tag{9}$$

For complete deformation ϵ, then, we have:

$$\epsilon = \frac{L - L_{(\epsilon_0=0)}}{L_{(\epsilon_0=0)}} \tag{10}$$

Using Equation (6), we finally obtain:

$$\epsilon = \frac{L}{L_0}(\epsilon_0 + 1) - 1 = (\epsilon_1 + 1)(\epsilon_0 + 1) - 1 = \epsilon_1 + \epsilon_1\epsilon_0 + \epsilon_0 \tag{11}$$

The dynamic losses in the test-specimen deformed by the impacts of the hammer are evidently measured from the angle of rebound in accordance with the equation:

$$\Delta W = mg\Delta H = 2mgr(\cos\varphi_1 - \cos\varphi_2) \tag{12}$$

where ΔH is the difference between the height of fall and the height of rebound of the pendulum hammer, and m is its effective mass.

It has been established that the dynamic losses of test-specimens not previously deformed are proportional to the square of the dynamic deformation, and when they are related to a unit volume of the deformed specimen, they do not depend on the thickness of the test-specimen. Hence, as an index of internal friction of the vulcanizate tested, we used in this case the coefficient:

$$K' = \frac{\Delta W}{V\epsilon_1^2} \tag{13}$$

In the general case, when a specimen previously deformed is tested, the empirical coefficient of internal friction is calculated from the equation:

$$K = \frac{\Delta W}{V\theta} \tag{14}$$

where

$$\theta = \frac{(\epsilon_1 + \epsilon_1\epsilon_0 + 2\epsilon_0)(\epsilon_1 + \epsilon_1\epsilon_0)}{1 + 2\epsilon_0} \tag{15}$$

It can be shown that θ is equivalent to the square of the dynamic deformation in the absence of static stress.

Designating the total work of dynamic deformation by W and taking as a first approximation the linear law of deformation, we have:

$$W = V\frac{E}{2}(\epsilon^2 - \epsilon_0^2) = V\frac{E}{2}(\epsilon + \epsilon_0)(\epsilon - \epsilon_0) \tag{16}$$

where E is the Young's modulus of the rubber.

The dynamic deformation is expressed by the equation:

$$\Delta\epsilon = \epsilon - \epsilon_0 \tag{17}$$

For the case $\Delta\epsilon = 1$, we have:

$$W_{(\Delta\epsilon=1)} = V\frac{E}{2}(1 + 2\epsilon_0) \tag{18}$$

Further, for the coefficient of specific losses, we have:

$$K = \frac{\Delta W_{(\Delta\epsilon=1)}}{V} = W_{(\Delta\epsilon=1)}\frac{\gamma}{V} \tag{19}$$

where γ is the relative hysteresis.

The modulus E can be determined from Equation (16):

$$E = \frac{2W}{V(\epsilon + \epsilon_0)(\epsilon - \epsilon_0)} \tag{20}$$

Combining Equations (20), (19), and (18), we have:

$$K = \frac{W(1 + 2\epsilon_0)\gamma}{V(\epsilon + \epsilon_0)(\epsilon - \epsilon_0)} \tag{21}$$

or, using the equation:

$$\gamma = \frac{\Delta W}{W} \tag{22}$$

we obtain finally:

$$K = \frac{\Delta W(1 + 2\epsilon_0)}{V(\epsilon + \epsilon_0)(\epsilon - \epsilon_0)} \tag{23}$$

Using for ϵ its value from Equation (11), Equation (23) can be represented in the form of (14) and (15).

In working out the method of the tests, it was established that the coefficient K for the first impact is always greater than for the succeeding ones, and a stationary value of the index is established after five repeated impacts. In order to obtain the best reproducibility in this work, the authors always used the value of the index for the fifth impact.

The coefficient K was measured for two effective weights of the hammer (500 and 250 grams) and for two angles of fall (90° and 120°). Specimens not previously deformed ($\epsilon_0 = 0$) and others deformed up to 50 per cent elongation ($\epsilon_0 = 0.5$) were tested. Higher values of static elongation could not be obtained because the test-specimens with high sulfur contents under these conditions were destroyed by the impacts.

MEASUREMENT OF THE EQUILIBRIUM STRESS

The value of the stress at equilibrium, which corresponds to the given deformation, was measured with a bulb dynamometer shown in the sketch in Figure 2. The basic advantages of the bulb dynamometer over those usually employed are: (1) its high sensitivity, which insures the absence in the apparatus of elements of dry friction; (2) its hermetic seal, which makes possible tests

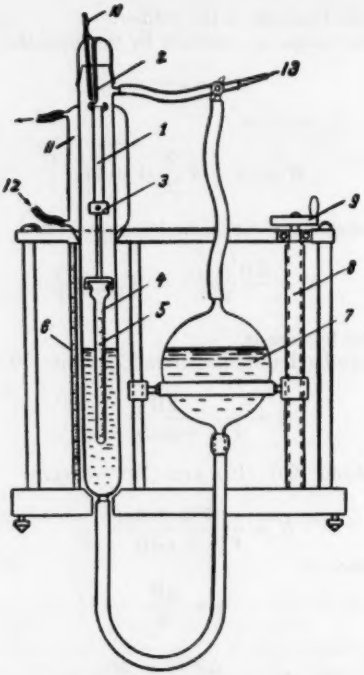

FIG. 2.—Float dynamometer.

1. Test-specimen
2. Upper clamp holder
3. Lower clamp
4. Dynamometer float
5. Stress scale
6. Displacement
7. Equalizing vessel containing mercury
8. Moving screw
9. Knob of moving screw
10. Thermometer
11. Thermostat jacket
12. Ultrathermostat
13. Vacuum and inert gas

in aggressive media, as well as under conditions which exclude chemical reaction with the medium (tests in vacuum and in inert gases), and (3) its simplicity of construction.

The work with the dynamometer was carried out thus. The specimen to be tested was placed between the clamps and the apparatus was hermetically sealed. Then, with a high-vacuum pump (BM-461) and a Langmuir pump (10^{-5} — 10^{-6} mm. Hg), the apparatus was evacuated for 10–12 hours. The apparatus was filled with nitrogen purified from all traces of oxygen by the

method described by Dogadkin and Pevzner[6] and with an ultrathermostat in the operating chamber a temperature of 70° C was obtained. Then the atmospheric medium was evacuated for the second time to the same vacuum of 10^{-5} — 10^{-6} mm. Hg, and the apparatus was again filled with nitrogen.

By gradually lowering the bulb, 7, the specimen was given the desired deformation and the zero time reading was recorded. The deformation was measured by the position of the dynamometer float 4 on the displacement scale 6 (see Figure 1).

Then the stress at the given deformation was measured. The stress was calculated by the relation:

$$\sigma = \frac{(Q - s\gamma h)g(\epsilon + 1)}{2S_0} \tag{24}$$

where σ is the stress calculated for a cross-section of the deformed specimen; Q is the weight of the dynamometer float; s is the square of the cross-section of the cylindrical part of the float; γ is the specific gravity of mercury; g is the acceleration of the force of gravity; S_0 is the area of the cross-section of the undeformed test-specimen; h is the depth of immersion of the float; and ϵ is the relative deformation.

The depth of immersion of the float, h, was measured by the position of the mercury level in the float chamber on the scale measuring the stress, which was brought up beside the dynamometer float. Then the stress corresponding to the particular deformation was measured periodically, after equal or increasing time intervals. In the alternate measurement of the rotation of the knob of the moving screw, 9, the equalizing chamber, 7, rises slowly until the dynamometer float has returned to the position corresponding to the particular deformation.

Next, the specimen was slowly cooled and heated. The temperature was varied within the limits of 30–70° C, and the stress was measured at the extreme temperatures. The coincidence of the values of the stress in successive cycles was taken as a criterion of the actual existence of equilibrium.

The method used is similar in principle to that described by Bartenev[3], who measured the equilibrium stress in rubber with a Poljani dynamometer without protecting the test-specimen from atmospheric oxygen.

EXPERIMENTAL DATA

The basic results of the measurements are summarized in Table 2 and shown in Figure 3.

The differences in the absolute values of the indexes of mechanical losses, measured by various methods, are an evident consequence of the differences in the nature, degree, and frequency of deformation to which test-specimens are subjected in the different methods. It is characteristic, however, that with all the testing methods used, the curves of the index of mechanical loss as a function of the content of combined sulfur are of the same nature. In the range of sulfur contents below approximately 9 per cent, the index of mechanical losses and, consequently, the internal friction of the vulcanizate, does not depend on the content of combined sulfur. Further absorption of sulfur causes a sharp increase of internal friction. The equilibrium modulus, E_∞, from the very beginning increases in proportion to the increase of the content of combined sulfur.

From the viewpoint of the fundamental purpose of the present study, it was interesting, using the experimentally obtained values of the equilibrium moduli,

to calculate the average molecular weights, M^*, of the chain segments between the bonds of the spatial network of vulcanizates with different contents of combined sulfur. Such calculations can be made on the basis of the statistical theories of elasticity, either of Wall and Treloar[7], or the more highly developed theory of Bartenev[8]. According to the data of Bartenev[8], in the range of stresses not exceeding 100 per cent, there are no essential differences between the values of M^*, calculated on the basis of either theory.

Before passing to the detailed calculations, it is necessary, however, to consider the fact that both statistical theories mentioned above were derived for a

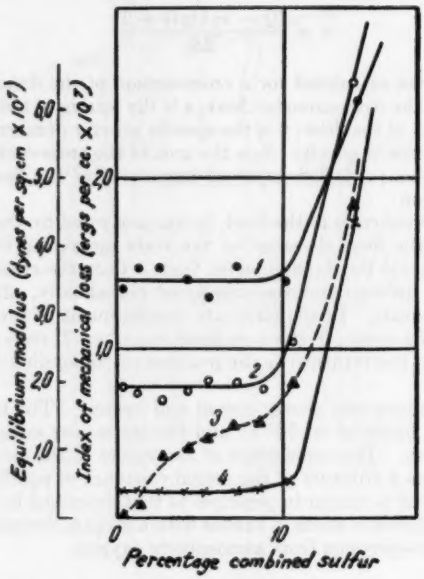

FIG. 3.—Index of mechanical loss and equilibrium modulus of vulcanizates as functions of the combined sulfur content.

1. $\pi E \tan \varphi$
2. $\frac{E(1-R)}{2}$
3. E_0
4. $\frac{\Delta W}{V\theta}$

so-called ideal rubber. In other words, the thermodynamic basis of the statistical theories is the entropy nature of rubberlike elasticity and the constancy of the internal energy of the deformation process.

The experiments of Bartenev[3] have shown that the ideal state of rubber, $\left(\frac{\partial u}{\partial \lambda}\right)_{P,T} = 0$, for soft butadiene-styrene vulcanizates is actually observed in the whole elongation range. At the present time, however, there are no data from the experimental study indicating that such a situation prevails also for hard rubber with a high content of combined sulfur.

An approximate estimation of the role of the energy and entropy components of the stress can be made, from the experimental study, by means of the ratio

of the equilibrium stress to the temperature at the given deformation. As was pointed out above, in the present study the equilibrium stress was measured at only two temperatures: 30° and 70° C. The data in Figure 4 do, nevertheless, offer some material for thermodynamic analysis.

If the equilibrium modulus is represented as the sum of the energy and entropy components in the form:

$$E_\infty = E_\infty(\Delta u) + E_\infty(\Delta S) \tag{25}$$

then by straight segments, marked in Figure 4 on the ordinate axis, it is possible to judge approximately the value of the energy component of the equilibrium modulus[3]. It can be seen that, in accordance with the data of Bartenev[3], this segment for vulcanizates which do not contain more than 8 per cent combined sulfur is near zero. Thus, soft vulcanizates satisfy the requirement of ideal conditions, and for them one of the above-mentioned statistical theories

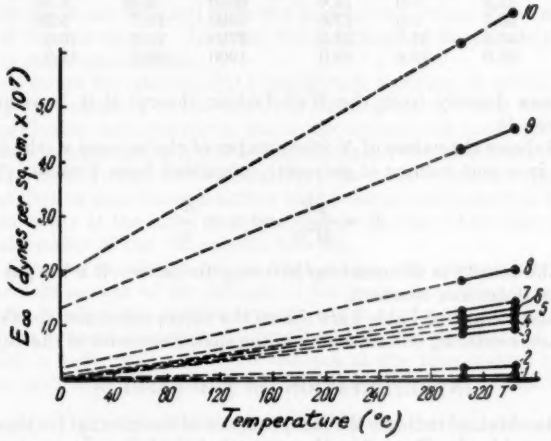

FIG. 4.—Linear extrapolation of the equilibrium modulus of vulcanizates containing different proportions of combined sulfur as a function of the temperature. (The figures on the graphs indicate the numerical order of the vulcanizates recorded in Table 1.)

can be applied directly. As for vulcanizates containing more combined sulfur, as is seen in Figure 4, for them the energy component of the modulus is already large and it is impossible to ignore it. For an approximate calculation of the molecular weight of a chain segment between the cross-linking of the spatial network of a vulcanizate, it is evidently necessary to take into account, not the total equilibrium modulus, but only its entropy component. The latter is calculated from the difference:

$$E_\infty(\Delta S) = E_\infty - E_\infty(\Delta u) \tag{26}$$

where the component $E_\infty(\Delta u)$ is determined, as was indicated above, from a segment indicated on the ordinate axis, in the linear extrapolation of the equation: $E_\infty = \psi(T)$. The value of M^* was calculated from the equation:

$$M^* = \frac{7}{2}\left(\frac{\rho RT}{E_\infty(\Delta S)}\right) \tag{27}$$

TABLE 3

INDEXES OF DENSITY OF SPATIAL NETWORK OF VULCANIZATES CONTAINING VARIOUS AMOUNTS OF BOUND SULFUR

Bound sulfur content (%)	E_∞ (dynes/sq. cm. $\times 10^9$) (70°)	E_∞ (Δu) (dynes/sq. cm. $\times 10^9$) (70°)	E_∞ (ΔS) (dynes/sq. cm. $\times 10^9$) (70°)	M^*	$N \cdot \frac{1}{cc.} \cdot 10^{19}$	$n \cdot \frac{1}{cc.} \cdot 10^{19}$	Number of atoms of bound sulfur in one cross-link of molecular network
0.40	0.61	~0	0.61	144800	0.39	0.20	36.1
1.28	2.45	~0	2.45	37800	1.61	0.75	28.4
2.73	9.18	~0	9.48	9860	5.77	2.88	16.7
4.29	10.8	~0	10.8	8660	6.57	3.28	23.7
5.60	12.4	~0	12.4	7480	7.61	3.80	25.3
7.44	13.1	~0	13.1	7120	7.99	3.99	32.8
8.89	13.6	~0	13.6	6830	8.33	4.16	37.7
10.02	20.1	2.5	17.6	5300	10.7	5.03	35.2
14.20	46.5	33.5	33.5	2790	21.3	10.6	23.7
26.55	68.0	49.0	49.0	1900	29.8	14.9	31.3

which follows directly from the Wall-Treloar theory[7] if it is assumed that $E_\infty = \sigma_\infty(\epsilon = 1)$.

Table 3 shows the values of N (the number of chains) and n (the number of cross-links in a unit volume of polymer), calculated from Formula (9):

$$N = \frac{\rho R}{M^* k} \text{ and } n \approx \frac{N}{2}$$

where ρ is the density in all cases near to 0.94 gram per cc.; R is the gas constant, and k is the Bolzmann constant.

In the last column of Table 3 are shown the values calculated for the number of sulfur atoms entering one cross-link of the spatial network of the vulcanizate.

INTERPRETATION OF THE RESULTS

The data obtained indicate the independence of the internal friction from the amount of combined sulfur, when the content of the latter does not exceed ~9 per cent. With a further increase of the combined sulfur content, a sharp increase of the internal friction of the rubber is observed.

From the viewpoint of the considerations given above, the independence of the internal friction from the combined sulfur content attests to the fact that the presence of the spatial chain in the vulcanizate does not essentially influence the nature of any heat motion of the chain segments between the cross-links. The same concept can be formulated as follows. The internal friction does not depend on the combined sulfur content as long as the mean distance between the cross-links of the molecular network exceeds the size of one segment, that is, an average segment of the molecular chain, which appears as a kinetic unit in the heat motion of the molecule. With a decrease of temperature as the chains become stronger, or stiffer, the molecular weight of the segment increases. This must be particularly great near the vitrification temperature, when the chains lose practically all their flexibility.

This latter fact must not be overlooked in a comparison of the results obtained in this work with well known data for the relation between the vitrification temperature and the content of combined sulfur[9]. In particular, the shift

of the vitrification temperature observed by Bartenev for natural-rubber vulcanizates toward higher temperatures with an increase of the content of combined sulfur, when the sulfur content does not exceed 4 per cent, does not contradict the data of the present work if one remembers that, at temperatures near T_g, the size of a segment can be of the same order as the length of the segment of the molecular chain between the cross-links of the spatial network, even with a very low sulfur content. Because of this, an increase of T_g is observed with an increase of the degree of vulcanization.

In the study of the change of the dielectric properties, measured at room temperature, with change of the combined sulfur content of rubber, an accelerated increase of the dielectric losses was observed; this reflects the great increase of internal friction with a combined sulfur content of the order 8–10 per cent[10]. The agreement between these data and those of the present work is evident.

The change of internal friction of a number of vulcanizates with increase of the combined sulfur content can be compared with those molecular-structural parameters which are obtained from the data for the values of the equilibrium modulus of these systems. However, the treatment of the results obtained in this part is more complicated.

Figure 5 shows the relation of the equilibrium modulus, as well as its energy and entropy components, to the combined sulfur content. As is seen, the bend on the equilibrium modulus curve, due to the appearance and further increase of the energy component, is found at approximately the same sulfur content at which the internal friction increases sharply. In other words, the rapid increase of internal friction and the appearance of the energy component of the equilibrium modulus are at the same combined sulfur content, which also determines the critical density of the vulcanizate network.

From this, the conclusion follows that rubber can exist in the ideal state only if the heat motion of the linkages of the molecular chains is not counteracted by the bonds of the spatial network which are formed during vulcanization. If this concept is correct, destruction of the "ideal" state of vulcanized rubber with a high combined sulfur content at the temperature in question takes place also with vulcanizates at lower states of vulcanization if they are

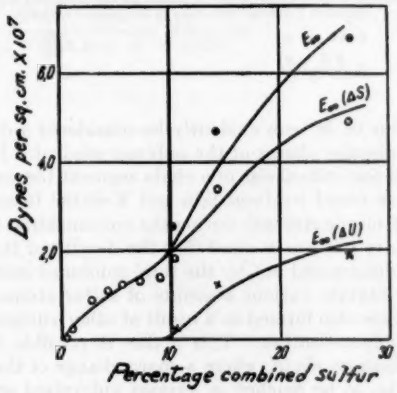

FIG. 5.—Equilibrium modulus E_∞ and its energy $E_\infty(\Delta u)$ and entropy $E_\infty(\Delta S)$ components as functions of the percentage of combined sulfur.

cooled to sufficiently low temperatures. This view can be experimentally verified by the temperature relation of the equilibrium stress, measured at the given deformation. The destruction of the ideal state, however, must take place at low temperatures which are near the vitrification temperature.

The relation between the internal fraction of rubber and the density of the spatial network of the vulcanizate, estimated from the value of the molecular weight M^* of a chain segment between the cross-links of the spatial network, is shown in Figure 6. From this figure it is seen that the critical value of M^*, which corresponds to the beginning of the dependence of internal friction on the degree of vulcanization, is ~7000, independent of the method of measurement employed.

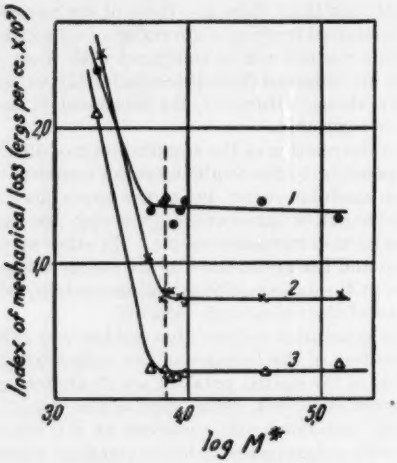

FIG. 6.—Relation of mechanical losses in rubber to the molecular weight of a chain segment between cross-links of the spatial network.

1. $\pi E \tan \varphi$
2. $\frac{E(1-E)}{2}$
3. $\frac{\Delta W}{V\theta}$

This critical value of M^* can evidently be considered a direct index of the flexibility of the molecular chains of the polymer studied. It is worth noting that such a value of the critical size of a chain segment between the cross-links of a vulcanizate was found by Dogadkin and Keifetz[11] from data on the dynamics of change of tensile strength during the vulcanization of natural rubber.

It is also necessary to keep in mind that the density of the spatial network of a vulcanizate is determined not by the total combined sulfur content alone. The sulfur bridges contain various amounts of sulfur atoms; chemical bonds between the chains are also formed as a result of other vulcanization processes, e.g., oxygen and polymerization. This makes it possible for the "critical" density of the vulcanizate chain, where a sharp change of the internal friction of the rubber sets in, to be reached in various vulcanized systems at various degrees of vulcanization.

CONCLUSIONS

1. The relation between the internal friction, which is responsible for heat formation during the dynamic deformation of unloaded vulcanizates of butadiene-styrene rubber, and the content of combined sulfur, which was changed within the limits of 0.5 to 26 per cent in the rubber, was studied.

2. It is shown that internal friction and the related relaxation properties do not depend on the percentage of combined sulfur up to 9.0 per cent. Further increase of the combined sulfur content causes a sharp increase of the internal friction of the rubber.

3. For the same vulcanizates of butadiene-styrene rubber, the equilibrium stress, as well as its energy and entropy components, were measured. It is shown that in vulcanizates which contain combined sulfur in proportions not greater than 8.0 per cent, the nature of the stress is predominantly entropic. Further increase of the combined sulfur content causes an increase of the energy component of the stress.

4. Proceeding from the values of the entropy component of the equilibrium stress, on the basis of the approximate theory of Wall, the values of the molecular weights of a chain segment between the cross-links of the spatial network M^* were calculated for vulcanizates containing varying percentages of combined sulfur.

5. It is shown that the value of M^* is 7000 for the polymer studied and is critical in the sense that further densening of the network causes a sharp increase of both internal friction and the energy component of the equilibrium stress. The hypothesis is advanced that the value of $M^*_{crit.}$ can be regarded as a criterion of the flexibility of the molecular chains of the polymer studied.

REFERENCES

[1] Gurevich and Kobeko, *Kauchuk i Rezina* **10**, 21 (1939).
[2] Dogadkin and Reznikovskii, *Kolloid. Zhur.* **13**, No. 1, 11 (1951).
[3] Bartenev, *Kolloid. Zhur.* **12**, No. 4, 241 (1950).
[4] Kornfeld and Poznyak, *Zhur. Tek. Fiz.* **3**, 4 (1939).
[5] Dillon and Gehman, *India Rubber World* **115**, 61, 217 (1946); RUBBER CHEM. & TECHNOL. **20**, 827 (1947).
[6] Dogadkin and Pevzner, "Studies of the Physics and Chemistry of Rubbers", Acts of the Sci. Res. Inst. of Tire Ind., 1950.
[7] Dogadkin, "Chemistry and Physics of Rubber". Goskimizdat (Gov. Chem. Pub.) **1947**, Chap. 8.
[8] Bartenev, *Zhur. Tek. Fiz.* **20**, No. 7, 858 (1950).
[9] Boyer and Stenser, Chemistry of Large Molecules, Gov. Press for Foreign Lit., Moscow, **1948**, No. 2, p. 9.
[10] Fuss, Gov. Press for Foreign Lit., Moscow, 1948, p. 265.
[11] Dogadkin and Keifetz, *Kolloid. Zhur.* **14**, 157 (1952).

CHEMIGUM SL—AN ELASTOMERIC POLYESTER-URETHANE *

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A great deal of interest has been aroused in recent years in isocyanate chemistry by the announcement of new elastomers based on diisocyanate modification of polyesters. Early du Pont patent literature[1] described diisocyanate modified alkyds, and Vulcaprene A, an elastomeric diisocyanate modified polyesteramide[2], has been offered to the rubber trade by Imperial Chemical Industries, Ltd., England. Several articles[3] also have been published on Vulcollan by Bayer and associates on work done in the laboratories of Fabenfabriken Bayer Co., Leverkusen, Germany.

More recently a new elastomeric polyester-urethane, Chemigum SL, was described[4] by the Goodyear Tire and Rubber Co. These rubbers are first made in the form of processible and storable raw gums, having many of the characteristics of pale crepe natural rubber. They can then be mixed on the mill or in the Banbury with additional curatives, such as diisocyanates and other compounding agents, and cured in standard rubber molds.

The cured physical properties of Chemigum SL are very similar to Vulcollan; both exhibit unusual toughness. Tensile strength is very high, as is resistance to cutting and chipping. Since the polyester-urethanes are saturated, cut-growth resistance is excellent. Even when cuts are initiated by sharp objects, there is no tendency to grow, even under stress. In this respect a vast superiority is shown over natural rubber or GR-S.

PREPARATION OF STORABLE CHEMIGUM SL

The preparation of the raw gum can be described by the following steps:

1. Preparation of the linear polyester.
2. Chain extension of the polyester with diisocyanate, giving the storable elastomer.
3. Cross-linking of the raw gum to give cured Chemigum SL.

The final vulcanizate physical properties are dependent upon many factors, the most important being the chemical structure of the starting materials and the molecular quantities of each component. In the preparation of the polyester, as shown:

$$HO—A'—OH \text{ (Glycol)}$$

and

$$HOOC—A—COOH \text{ (Dibasic Acid)}$$

give

$$HO—A'—OOC—A—COO—A'—OH + H_2O$$

(Polyester)

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 45, No. 11, pages 2538-2542, November 1953. Three photographs are omitted. The paper was presented at the meeting of the Division of Rubber Chemistry, American Chemical Society, Boston, Mass., May 27-29, 1953.

there is considerable latitude in the choice of glycols and dibasic acids as well as molar ratios of reactants in case a mixture is desired. Depending on the specific glycols and dibasic acids selected and the molar ratios desired to make a polyester, it is possible to obtain finally a cured elastomer that does not harden or crystallize on aging, yet exhibits outstanding physical properties.

Since it is necessary to have the polyester segment terminated in hydroxyl groups, an excess of glycol is used when reacted with adipic acid. In this way, also, the degree of polymerization or molecular weight of the polyester can be controlled within optimum limits so that elastomeric products result in the reaction with diisocyanates.

The effect of dibasic acid structure on the physical properties of Vulcollan is shown in Table I as described by Bayer[5]. Adipic acid yields nonhardening

TABLE I

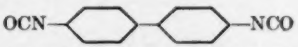
EFFECT OF DIBASIC ACIDS ON PHYSICAL PROPERTIES OF VULCOLLAN[5]

Glycol	Acid	Tensile strength (kg./sq. cm.)	Elongation (%)	Remarks
Ethylene	Succinic	273	625	Hard, leathery
Ethylene	Adipic	350	640	Slowly hardens
Ethylene	Sebacic	—	—	Hardens immediately
Ethylene	Diglycolic	270	570	Leathery
Ethylene	Phthalic	107	261	Glass-hard without softener
1,2-Propylene	Succinic	180	670	Leathery
1,2-Propylene	Adipic	220	780	Does not harden
2,3-Butylene	Adipic	179	630	Does not harden

rubbers. Short-chain acids as well as aromatic acids, such as phthalic, yield hard, leathery products.

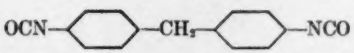
The process of polyaddition, which in principle is the addition of diisocyanates to dihydroxy and polyhydroxy compounds and to other compounds containing two or more reactive hydrogen atoms, makes it possible to synthesize, from small molecules, products of high or even extremely high molecular weight, and with practically predetermined structures and properties.

The structure of the diisocyanate used in the chain extension step contributes markedly to the cured physical properties. The diisocyanates used in the preparation of storable rubbers are:

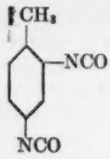


4,4'-Xenylene diisocyanate (XDI)

1,5-Naphthalene diisocyanate (NDI)



Methylene bis(4-phenylisocyanate) (MDI)



2,4-Tolylene diisocyanate (TDI)

symmetrical aromatic diisocyanates, which are preferred over aliphatic diisocyanates.

In the second step in the preparation of the rubber, the polyester segment is "chain extended" with diisocyanate as follows:

OCN—R—NCO (Diisocyanate)

and

HO—A′—OOC—A—COO—A′—OH

(Polyester)

give

HO—Polyester—OCONH—R—Polyester—O

Melted polyester at 120° C is mixed with the appropriate amount of diisocyanate until thoroughly blended. Polymerization can be completed either in an internal mixer or by heating the blend in shallow trays in an oven.

As was stated earlier, the nature of the modified polymer will depend on the amount of diisocyanate used to chain-extend and cross-link the polyester. It has been discovered that the production of a processible storable rubberlike polymer involves, not only the determination of the critical amounts of diisocyanate to be used, but also a given range does not apply to all diisocyanates.

The critical amount of diisocyanate to be used can be estimated by the relation:

$$\frac{\text{Moles of diisocyanate}}{\text{Moles of polyester}} = R \text{ value}$$

The most useful range is from 0.70 to 0.99 for optimum storability and processing. Thus, molecular weight is controlled by the amount of excess polyester used.

Typical physical properties of the raw gum are summarized in Table II.

TABLE II

PHYSICAL PROPERTIES OF STORABLE RAW GUM

Specific gravity	1.17
Softening range (° F)	284–365
Mooney (ML-4 at 212° F)	50–100
Olsen flow (212° F; 500 lb. per sq. in.), sec./in.	120–200
Intrinsic viscosity [η]	1.0–2.0
Molecular weight	25,000–50,000
Gel (%)	0–10
Soluble as 20% cements ketones (MEK), esters, and chlorinated hydrocarbons	
Storage without crystallizing (months)	6–12

EFFECT OF *R* VALUE ON PHYSICAL PROPERTIES OF RAW GUMS

The effect of increasing the molar ratio of diisocyanate to polyester (*R* value) is shown graphically in Figures 1, 2, 3, and 4. As the molecular weight of the raw gum increases, dilute solution viscosity, Olsen flow time, Mooney, and softening point all increase.

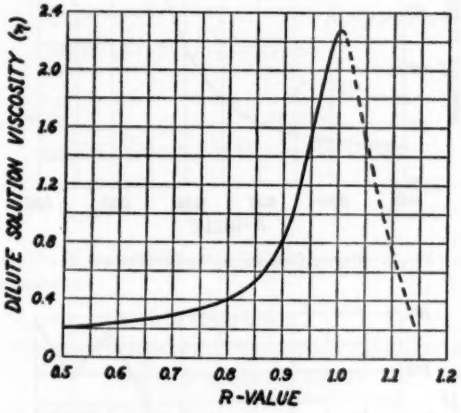


FIG. 1.—Dilute solution viscosity *vs.* *R*-value Chemigum SL.

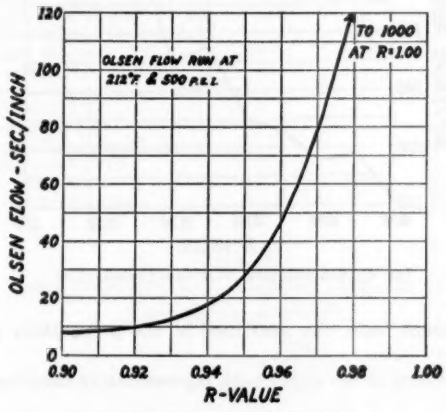


FIG. 2.—Olsen flow *vs.* *R*-value Chemigum SL.

THE CROSS-LINKING REACTIONS

The high molecular-weight, storable rubbers contain the following nitrogen linkages in addition to the ester links: urethane, urea, and amide. Later these serve as cross-linking points as the additional diisocyanate reacts with the nitrogen hydrogen atoms. The diisocyanates used as curatives may be the

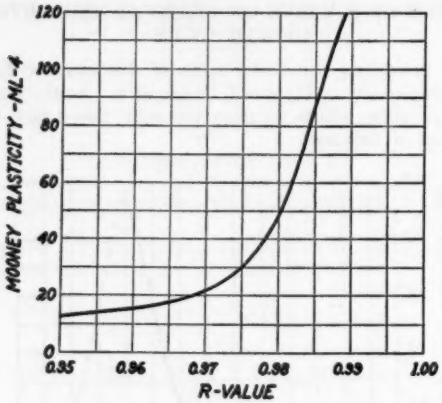


FIG. 3.—Mooney plasticity *vs.* *R*-value Chemgum SL.

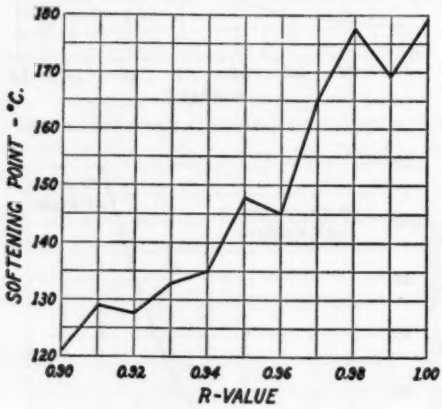


FIG. 4.—Softening point *vs.* *R*-value Chemigum SL.

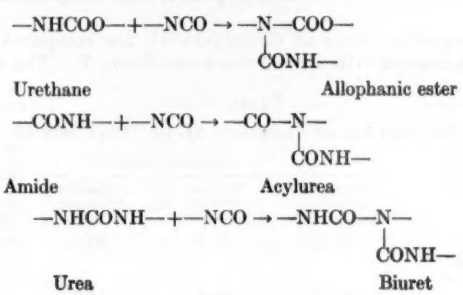
same as, or different from, the ones used in the preparation of the storable rubber.

Typical elastomers in use today with representative curatives are:

Rubber	Curatives
Natural, GR-S	Sulfur + accelerator
Neoprene	Metallic oxides
Hypalon S-2	Metallic oxides or diamines
Acrylate	Metallic oxides or amines
Thiokol	Metallic oxides
Chemigum SL	Diisocyanates

Polyester-urethane rubbers are cross-linked by an entirely different type of chemical reaction. These reactions begin as soon as additional isocyanate curative is added to the millable raw gum.

The isocyanate cross-linking reactions are



Of the three major diisocyanate cross-linking reactions, the ones with amide and urea predominate.

TABLE III

PHYSICAL PROPERTIES OF VULCANIZED CHEMIGUM SL

(Cured 15 minutes at 280° F)

Tensile strength (lb./sq. in.)	5450
Hot tensile at 200° F (lb./sq. in.)	2860
Elongation (%)	750
Hot elongation at 200° F (%)	845
Modulus (300%) (lb./sq. in.)	675
Hardness (Shore A)	65
Hot cut flex (min.)	300
Bureau of Standards abrasion (Index = 100)	200
Hot rebound (%)	84
Cold rebound (%)	80
Schopper tear (nicked) (lb./sq. in.)	2000
Freezing point (° C)	−35
Ozone resistance	Excellent
Ultraviolet resistance	Excellent

TABLE IV

AGED PROPERTIES OF VULCANIZED CHEMIGUM SL

(Cured 15 min. at 280° F)

	Tensile strength (lb./sq. in.)	Elongation (%)
Aged in dry heat		
30 days at 158° F	4700	685
14 days at 250° F	500	580
Aging in water		
3 months at 77° F	5000	—
2 days at 200° F	1700	—
14 days at 158° F	1000	—

PHYSICAL PROPERTIES OF CURED CHEMIGUM SL RUBBERS

Typical physical properties of vulcanized Chemigum SL are shown in Tables III and IV.

As shown by these data, resistance is poor to high temperatures, hot water, and steam.

Dynamic properties of cured Chemigum SL are compared with natural rubber and oil-extended GR-S tread stocks in Table V. The data were ob-

TABLE V

PERFORMANCE OF CHEMIGUM SL IN TREAD STOCKS

Rubber stock	Dynamic properties			
	Dynamic modulus (kg./sq. cm.)	Internal friction (kilopoises)	Dynamic resilience (%)	Relative heat generation
Chemigum SL	84.4	15.9	63.3	65
Chemigum SL plus 30 part MPC black	196.0	49.1	54.5	128
Natural rubber tread	91.8	35.1	39.6	109
Oil-extended GR-S tread	116.0	59.3	29.0	141

tained by means of the Goodyear Vibrotester. Polyester rubber compares favorably with standard tread stock, having higher resilience and generating less heat on flexing than the hydrocarbon rubbers.

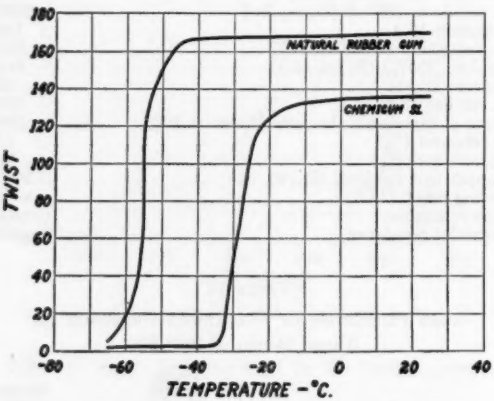


FIG. 5.—Cold hardening of Chemigum SL. Gehman Twist Method.

Another disadvantage of these polymers is the tendency to harden at low temperatures. Figure 5 illustrates cold properties as measured by the Gehman twist method. Chemigum SL freezes at −35° C, compared with −65° C for cured natural rubber gum.

Fillers, such as carbon blacks, and nonblacks such as clays, may be employed, but with very little enhancement of physical properties except for certain rubbers that have low initial properties. In such rubbers, considerable

amounts of black may be used to advantage. Normally there is a decline in physical properties with the addition of standard fillers; 300 per cent modulus and hardness increase with increased loading.

TABLE VI

OXYGEN ABSORPTION

Time (hours)	O_2 Absorbed (cc. per gram of Polymer at 100° C)		
	Natural rubber tread stock[a]	GR-S tread stock[a]	Chemigum SL
0	0	0	0
40	10	4	0.32
80	27	10	0.48
120	58	14	0.56
160	92	18	0.64
240	—	27	0.88
320	—	36	1.04
450	—	—	1.36
910	—	—	2.24

[a] Natural rubber and GR-S tread stocks contain 45 parts of carbon black per 100 parts of rubber and 1.25 parts of *N*-phenyl-*β*-naphthylamine as antioxidant.

Oxygen absorption data are shown in Table VI. Oxygen absorption for typical natural-rubber tread and GR-S tread stocks is appreciable at 100° C after 300 hours. After 910 hours, only 2.24 cc. of oxygen per gram of Chemigum SL was absorbed.

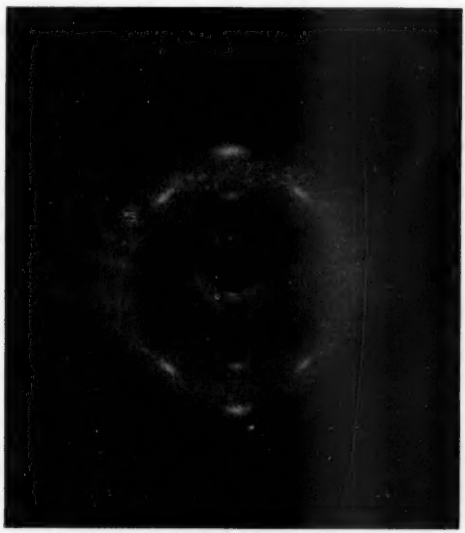


FIG. 6.—Natural rubber gum stock stretched 400%.

The x-ray pictures in Figures 6 and 7 show the similarity of Chemigum SL to cured natural-rubber gum stock when both are stretched 400 percent. The Chemigum SL pattern disappears when relaxed.

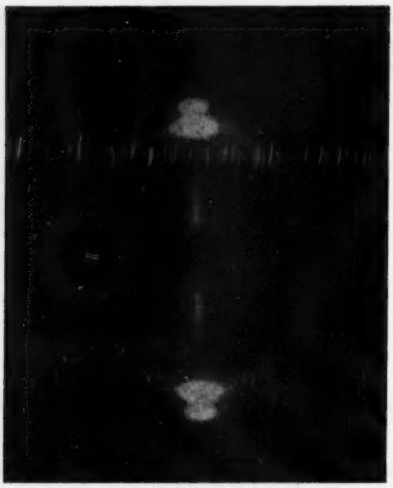


FIG. 7.—Chemigum stretched 400%.

APPLICATIONS

A great deal of work has been done in developing uses for elastomeric polyester-urethanes. Potential uses include wear resistant veneers on pneumatic tires. Solid tires have given outstanding performance on electric lift trucks. A high degree of cut resistance is exhibited. Soles, heels, belt surfaces, and floorings may be protected by localized application of wear resistant Chemigum SL.

Since the raw gum stocks are readily soluble in standard solvents, they lend themselves to cement compounding and find use as protective coating on rubber, plastics, and fabrics. A solution of Chemigum SL sprayed on the surface of rubber or plastic gives an adherent, flexible, and scuff-resistant coating that is at the same time resistant to sunlight, ozone, and general weathering.

ACKNOWLEDGMENT

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REFERENCES

[1] Rothrock, U. S. patent 2,282,827 (May 12, 1942); Hanford and Holmes, U. S. patent 2,284,896 (June 2, 1942); Christ and Hanford, U. S. patent 2,333,539 (Nov. 9, 1943).

[2] Harper, Smith, and White, *Proc. 2nd Rubber Technol. Conf. London*, **1948**, p. 61; RUBBER CHEM. & TECHNOL. **23**, 608 (1950).

[3] Bayer, *Ann.* **549**, 286 (1941); *Angew. Chem.* **59**, 257 (1947); Hebermehl, *Farben, Lacke, u. Anstrichstoffe* **8**, 123 (1948); Petersen, *Ann.* **562**, 205 (1949); Bayer, Müller, Petersen, Piepenbrink, and Windemuth, *Angew. Chem.* **62**, 57 (1950); RUBBER CHEM. & TECHNOL. **23**, 812 (1950); Brenschede, *Z. Elektrochem.* **54**, 191 (1950); Hochtlen, *Kunststoffe* **40**, 221 (1950); **42**, 303 (1952); Müller, Bayer, Petersen, Piepenbrink, Schmidt, and Weinbrenner, *Angew. Chem.* **64**, (1952); Müller, U. S. patent 2,620,516 (Dec. 9, 1952); Schmidt, U. S. patent 2,621,166 (Dec. 9, 1952); Siefken, *Ann.* **562**, 75 (1949); Popper, *Rubber Age* (N. Y.) **73**, 81 (1953).

[4] Seeger, U. S. patents 2,625,531 and 2,625,532 (Jan. 13, 1953); Mastin and Seeger, U. S. patent 2,625,535 (Jan. 13, 1953); *Rubber Age* (N. Y.) **73**, 90 (1953).

[5] Bayer, Müller, Petersen, Piepenbrink, and Windemuth, *Angew. Chem.* **62**, 57 (1950); RUBBER CHEM. & TECHNOL. **23**, 812 (1950).

SURFACE CONDITION AND ELECTRICAL IMPEDANCE IN RUBBER FRICTION *

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INTRODUCTION

Evidence has been advanced recently[1] that the frictional force between rubber and a hard smooth track is proportional to the true area of contact between rubber and track, the area depending on the deformation of the asperities on the surface of the sample under the influence of the normal load. It is to be expected that, during sliding, the asperities undergo an additional deformation as a consequence of the tangential stress. Direct observation of the interface rubber-track is difficult, but it was thought that, if the rubber could be made electrically conductive, there should be detectable changes in the electric resistance between sample and track when the rubber is set into motion. Electrically conductive rubber is easily produced by incorporating carbon black in the compound, and the results obtained with such specimens are reported here. Great interest attaches to carbon-loaded rubbers for their own sake as practically all rubber tires contain about 30 per cent by weight of carbon black.

EXPERIMENTAL

The equipment used for these experiments was the same as in the earlier investigation[2]. Each sample, 3.17 mm. thick and 4.7 sq. cm. in area, was bonded to a steel plate which served as one electrode. The other electrode was the track, made of chromium-plated brass, over which the sample slid at a velocity of 0.00216 cm. sec.$^{-1}$, and under a normal load of 3.96 kg. The track was cleaned according to a standard technique with acetone after each run. The composition of the samples was as follows: rubber 100, zinc oxide 5, sulfur 2.5, Santocure (accelerator) 0.5, Philblack O (furnace black) 50.0, stearic acid 2.5, pine tar 4.5, phenyl-β-naphthylamine (antioxidant) 1.0. This recipe represents a typical tire tread compound. The samples were cured at 140° C for 40 minutes, and their sliding surface was molded against a ground-glass plate.

The first measurements were carried out with a d.c. potential applied between sample and track, but it was found that the results were subject to time effects and that the samples did not obey Ohm's law. For this reason the experiments were continued with low-frequency alternating current. As will be shown later, Ohm's law was still not followed at these frequencies, but the deviations from linearity in the current-voltage curves were relatively unimportant, and measurements could be made within a narrow range of voltages, which were kept constant in each individual run. The frequencies employed were 21 c/s and 110 c/s. These particular values were dictated, on the low-frequency side by availability, and on the high-frequency side by the endeavor

* Reprinted from the *Proceedings of the Physical Society*, Vol. B 66, pages 817–825 (1953).

to keep clear of the region of anomalous dielectric dispersion[3]. The alternating currents were measured by means of a valve voltmeter shunted by resistances of suitable values.

The ratio of potential difference to current will be referred to as impedance R, although this term may be slightly misleading in view of the nonlinearity of the phenomena.

IMPEDANCE CHANGES DURING SLIDING

When a new sample is put on the track and is loaded normally, the impedance decreases and reaches a constant value after a few hours. For this reason the samples were left on the track for at least 12 hours before measurements commenced. The equilibrium current-voltage characteristics at the two frequencies are shown by curves I in Figure 1 (*a*), which demonstrate the extent to which Ohm's law is not obeyed by this material. The higher current at the

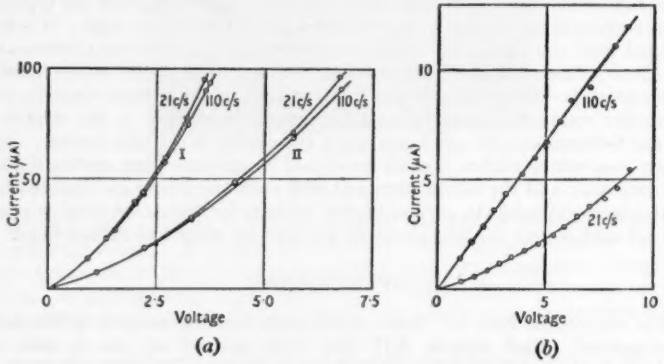

FIG. 1.—(*a*) Current-voltage characteristics of resting sample: I, when new; II, three days after completion of experiment. (*b*) Current-voltage characteristics of sliding sample after application of d.c. potential.

lower frequency found under these conditions is most probably due to residual inductance in the leads and measuring equipment, since the same effect was observed when the sample was replaced by an ohmic resistor. The corresponding difference in the nominal value of the impedance is small compared with effects observed during sliding.

During sliding, the following measurements were made. The frictional force was read every 30 seconds, and at the same instants the impedances were determined, alternating measurements at 21 c/s and 110 c/s, so that the readings at each frequency were spaced at one minute intervals. The travel of the sample was determined at suitable times.

The results obtained with a new sample are given in Figure 2 (*a*), the impedance measurements having been made at a potential difference of 4.08 v. There is no material difference between the impedances at 21 c/s and 110 c/s, but they reverse their order during the initial stages of the experiment, so the low-frequency value becomes larger than the impedance at the higher frequency. The character of the impedance curves is very similar to that of the frictional force curve.

When the drive is switched on (time zero), the frictional force increases sharply, while the slack is taken up in various parts of the apparatus, mostly in the towing lines. There is a similar increase of the impedances during this period, and a point of inflection is found in all curves when static friction is overcome and the sample begins to move. The similarity in the time-dependence of the three quantities is also maintained in such details as the sigmoid range following shortly after the point of inflection. Finally, both frictional force and impedances become essentially constant, the latter after having passed through an ill-defined maximum.

The sample does not immediately move with the prescribed constant velocity, but starts at a slower rate and accelerates until the slack has been com-

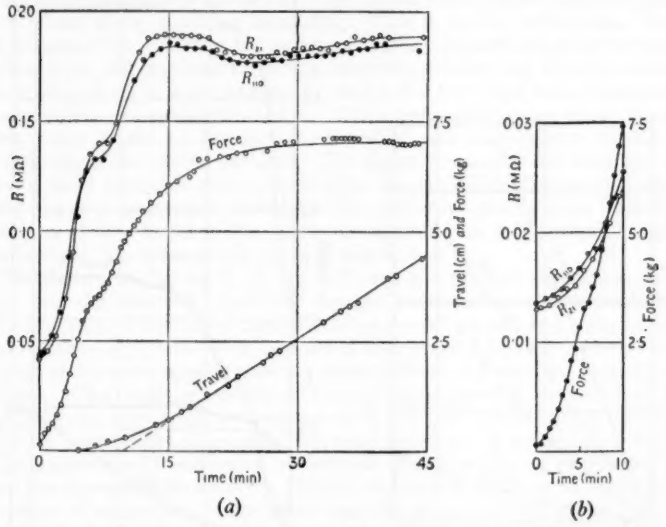

FIG. 2.—(*a*) Impedances *R*, frictional force and travel of a new sample plotted against time. Applied voltage 4.08 v. (*b*) Impedances of, and shearing force on, rubber sandwiched between two bonded plates plotted against time. Applied voltage 1.61 v.

pletely taken up. The maximum of the impedance curves appears to coincide with the region of the travel curve where the sample reaches constant velocity.

The changes of the impedance described above are only partially reversible. When the sample is stopped, the impedances decrease slowly but, as curves II of Figure 1 (*a*) show, they have still 2.5 times their original value after a lapse of 3 days.

Assuming that the effects shown by these experiments have their origin partly in the bulk of the rubber, and partly in the surface asperities, it is essential to assess the contribution to the effects by the deformation of the bulk material. For this purpose a sample was used which had approximately the same dimensions as the friction sample but was bonded between two steel plates, the lower one of which was fixed to the track and the upper one to the carriage usually holding the friction samples. The result of subjecting this sandwich to shearing stress is shown by Figure 2 (*b*). The force rises, of

course, much faster than when the sample can move; the absolute values of the impedances and their relative increases at comparable values of the stress are considerably lower than those of the friction sample.

A simple variant of the experiment is to repeat the measurements after the rubber surface has been abraded. This was done by running the sample a few times over silicon carbide cloth[4], changing the direction of motion after each run in order to prevent the formation of an abrasion pattern[5]. As with a new sample, some time is required for the rubber to settle down after abrasion, and curves *a* in Figure 3 give the current-voltage characteristics after 24 hours.

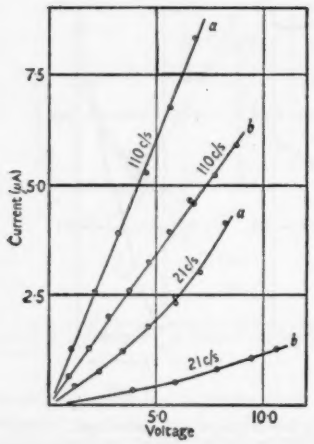

FIG. 3.—Current-voltage curves of abraded sample: (a) resting sample, one day after abrasion; (b) during sliding, after application of d.c. potential.

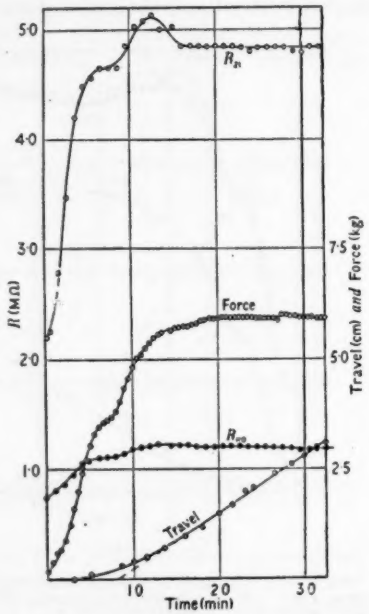

FIG. 4.—Impedance *R*, frictional force and travel of abraded sample plotted against time. Applied voltages: at 21 c/s, 5.6 v; at 110 c/s, 4.0 v.

Abrasion affects the conductive behavior of the sample profoundly. The impedance has increased one to two orders of magnitude, depending on the frequency. At 110 c/s the current is far larger than at 21 c/s and obeys Ohm's law within the limits of experimental error. The results obtained when the sample slides are given in Figure 4. The frictional force increases in the same manner as before, but the equilibrium value is about 15 per cent lower than in the case of the new sample. From this may be deduced that the true area of contact has been reduced by a similar amount.

The trend of the impedances curves in Figure 4 is also the same as before, but the relative increase at 110 c/s is very small compared with that at 21 c/s.

The table gives equilibrium values of the relative increases of the impedance in the four instances described in this section.

RELATIVE INCREASE OF IMPEDANCE DURING SLIDING

Frequency (c/s)	21	110
New sample	350%	330%
Abraded sample	230%	64%

It will be seen from this table that the effect is reduced by abrasion.

DISCUSSION OF SLIDING EXPERIMENTS

After the sample has started to move in the experiments described above, the frictional force continues increasing. This is due to two causes. In the first instance rubber friction has an approximately logarithmic positive velocity coefficient[6], so the frictional force rises until the velocity has become constant. In addition, there is a mechanism by which the frictional force increases for some time, even at constant velocity. This is a sluggish process which depends, among other things, on the distance travelled, and is thought to be due to a conditioning of the rubber surface[7]. The sigmoid region of the frictional force curve is most probably the outcome of a superposition of these two effects. There may yet be another reason for this particular phenomenon because an indication of it is found in the stress curves of Figure 2 (*b*), which suggest a peculiarity in the stress-strain curve of the rubber.

Comparison of Figures 2 (*a*) and 2 (*b*) and the effect of abrasion appear to prove that the observed impedance changes have their origin preponderantly in the top layer of the rubber nearest the track, and are caused by the deformation of surface asperities which, because of their smaller combined cross-section, undergo at the same applied shearing stress a larger deformation than the bulk material. The conditions on the surface are complicated by the fact that there are abrupt changes in the cross-section of the electric conductor; in the transition from bulk rubber to asperity, the total resistance is not equal to the sum of the geometrically calculated resistances, but there is an additional term called the spreading resistance[8]. Similar arguments apply to the impedance. The order of magnitude of the effect may be gauged by the simple case of a cylindrical asperity of equal diameter and height resting on a highly conductive track. The spreading resistance r at the junction of a small cylinder of radius a with an infinitely extended conductor is $r = \rho/4a$, where ρ is the specific resistivity of the material and amounts in the present instance to about 28 per cent of the total resistance. If the asperity is strained during sliding, its cross-section will most probably be reduced, and it will be seen that, in this case, the spreading resistance will increase. The conclusion drawn from these considerations is that the spreading resistance or impedance will enhance any effects due to deformation of the asperities.

The results obtained with the new sample will be dealt with in detail first. If this rubber were an ordinary, though poor, conductor of electricity, the deformation of the asperities would by itself lead to an increased resistance by a 'strain gauge' effect. However, rubbers of the tire tread type are not ordinary conductors, but their conductivity is highly strain sensitive[9]. This behavior is generally attributed to continuous, though open, carbon structure extending over large regions of the compound and readily breaking on straining the rubber[10]. To estimate the amount of the strain of the asperities necessary to

produce impedance changes of the order of those shown in Figure 2 (*a*), a cylindrical sample of 2.54 cm. diameter and 1.27 cm. height, bonded to steel plates, was extended and its impedance measured. The strain in this experiment is not well defined, but may be considered as approximating to that of a simple extension. It was found that an extension of only 19 per cent sufficed to increase the impedance by 350 per cent, and a rough estimate shows that the same change of impedance could be brought about by a simple shear of about 35 per cent, the angle of shear being slightly more than 19°.

During sliding, the passage of alternating current through the sample ceases to be purely conductive as the impedance at 21 c/s exceeds that at 110 c/s. This behavior indicates, of course, that a displacement current flows through the sample and that the total current is no longer the sole result of electronic and ionic conduction, or of the migration of other carriers of electricity.

With the abraded sample large local deformations occur on the abraded surface[11], and the breakdown of the carbon structure brought about thereby is more pronounced than that brought about by the comparatively small strain occurring on the surface of a new sample during sliding. The top layer of the abraded rubber may be visualized as a dielectric containing well dispersed and immovable conductive carbon particles, which increase the dielectric constant of this layer, and discrete electricity carriers. The relative magnitude of the capacitive and conductive currents depends on the frequency, and at 110 c/s the contribution of the conductive current to the total current appears to be small because of the linearity of the current-voltage curve in Figure 3. The nonlinearity of the corresponding curve at 21 c/s, like that of the curves in Figure 1, seems to show that the motion of the electricity carriers is not governed by Stokes' law.

As the conductive part of the current is confined to a path along the deformed asperities, but the capacitive current can pass from the solid back of the sample to the track by the dielectrically shortest way, it is not surprising to find that the impedance changes shown in Figure 4 should be greater at 21 c/s than at 110 c/s.

THE EFFECT OF A D.C. POTENTIAL

If the top layer of high electric impedance postulated in the last section exists, the following effect may be predicted. When a d.c. potential is applied between sample and track, practically the whole voltage drop should take place across this top layer and thus give rise to a high electric field strength and to electrostatic attraction between sample and track, with a corresponding increase of the frictional force.

The results of such experiments are given in Figure 5 for a new sample, and in Figure 6 for an abraded sample. Relatively low voltages suffice for the production of substantial effects, a voltage of 240 v, for example, increasing the frictional force by nearly 50 per cent.

On switching on the d.c. potential, the frictional force does not immediately rise to its final value. Within the first one or two minutes the frictional force rises quickly and then continues increasing at a lower rate for at least 30 minutes (*cf.* Figure 6) before it becomes constant.

These and other time effects, shown in Figures 5 and 6, are almost certainly connected with the time dependence of the direct current flowing through the sample. The current decreases rapidly after being switched on; during the first five minutes it drops to about one-third, and then becomes constant at one-tenth, of the initial value. It is thought that the declining current is due

to the exhaustion of ions or other carriers of electricity in the top layer, thus leading to a higher resistance and higher field strength across the sample. That the passage of direct current produces a physical change in the sample is demonstrated by its subsequent behavior towards alternating voltages. The changes brought about by the direct current are most pronounced in the new sample where, as Figure 1 (*b*) shows, the impedance is increased many times and has become frequency dependent. The effect is similar but not so pronounced in the abraded sample, as seen in Figure 3. These findings are com-

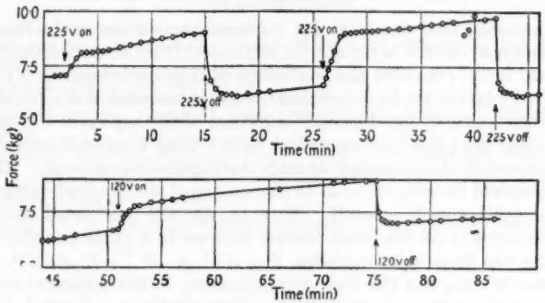

FIG. 5.—The effect of d.c. potentials on the frictional force of a new sample plotted against time.

patible with the view that the number of electricity carriers has been reduced by the direct current.

Electrostatic attraction can be shown by another, rather striking, method. Because of the positive velocity coefficient of rubber friction, rubber can be made to slide along a track under constant tangential stress[7]. If this is done with a sample of tire-tread rubber, application of a d.c. potential stops the sample instantaneously.

The electrostatic force does not, in principle, depend on the process of sliding, and it should be possible to demonstrate it with a resting sample of abraded

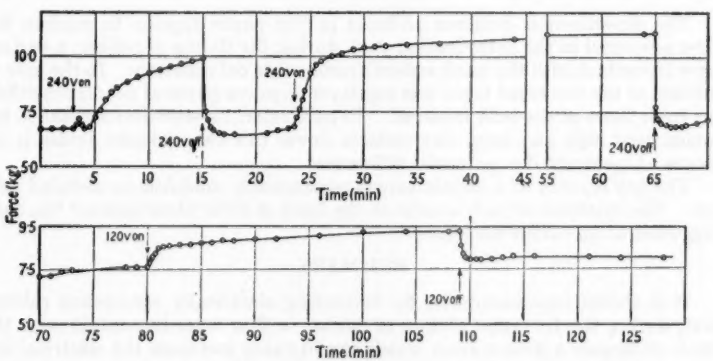

FIG. 6.—The effect of d.c. potentials on the frictional force of an abraded sample plotted against time.

rubber where, it has been pointed out, a permanent modified top layer exists. The difficulties in this experiment are the same as those encountered when the welded bridges between contiguous pieces of metal are to be evinced directly[12]; local contacts between sample and track must all be equally maintained while the normal load is removed. It has been found possible to make rubber adhere electrostatically to metal, but the results depended very much on the manipulative skill of the experimenter.

THE THICKNESS OF THE TOP LAYER

If it is assumed that the total d.c. voltage drop occurs in the top layer, the effective thickness of this layer can be estimated from the observed increase of the frictional force, provided the coefficient of friction is known. The difficulties in this calculation are to determine the exact increase of the frictional force, and to find the value of the dielectric constant of the top layer. Figures 5 and 6 make it clear that equilibrium values take a long time to establish, and the physical properties of the sample change during the experiment. The electrostatic force should be proportional to the square of the applied voltage, but the data do not quite give this result. Fortunately, the calculated thickness does not depend critically on the other factors because in a plane parallel condenser, to which the top layer approximates, $d = 6.71 \times 10^{-7} (\epsilon V^2 A/N)^{\frac{1}{3}}$, where d is the thickness in cm., ϵ is the dielectric constant, V the potential difference in volts, A the area in sq. cm., and N the electrostatic, i.e. normal, force in kg. According to Figure 6, 240 v give an increase of the frictional force of about 3.6 kg. The coefficient of friction in this region is 1.9, so that the normal load has increased by about 1.9 kg. With these figures $d = 8.03 \times 10^{-4} \epsilon^{\frac{1}{3}}$ cm. If the carbon black were dispersed as isolated spheres, the theoretical value of the dielectric constant of the top layer would be about 4, the dielectric constant of the rubber hydrocarbon taken to be equal to 2.4. If the original carbon structure survived in the form of short rods with the average length to diameter ratio 4/1, which is a likely value, the dielectric constant (Sillars 1937) should be about 10. The order of magnitude of the thickness of the top layer is therefore a few thousandths of a centimeter.

CONCLUSIONS

The experimental evidence adduced in this paper appears to confirm the view advanced in the Introduction that, during the sliding of rubber, a surface layer in contact with the track suffers considerable deformation. In the case of rubbers of the tire tread type, this top layer acquires physical properties different from those of the bulk material. In particular, its electrical resistance becomes very high and large electrostatic forces can be produced across it by means of moderate d.c. potential differences.

The top layer is to a certain extent permanently modified on abraded rubber. The existence of such a layer on the basis of other observations[5] has been suggested at an earlier occasion.

SUMMARY

It is shown experimentally, by employing electrically conductive rubber, that, during the frictional gliding of rubber, a thin layer in contact with the track undergoes a deformation which considerably increases the electrical impedance of this layer. In the case of previously abraded rubber, the layer is permanent. If a d.c. potential is applied between sample and track during

sliding, electrostatic attraction between sample and track is produced, and this increases the frictional force. The thickness of the layer, estimated from the magnitude of the electrostatic force, is a few thousandths of a centimeter.

ACKNOWLEDGMENT

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REFERENCES

[1] Schallamach, *Proc. Phys. Soc.* B **65**, 657 (1952).
[2] Roth, Driscoll, and Holt, *Bur. Standards J. Research* **28**, 439 (1942); Schallamach, *Proc. Phys. Soc.* B **65**, 657 (1952).
[3] Schallamach, *Trans. Inst. Rubber Ind.* **27**, 40 (1951).
[4] This silicon carbide cloth was John Bull No. 50.
[5] Schallamach, *Trans. Inst. Rubber Ind.* **28**, 256 (1952).
[6] Roth, Driscoll, and Holt, *Bur. Standards J. Research* **28**, 439 (1942); Schallamach, *Proc. Phys. Soc.* B **66**, 386 (1953).
[7] Schallamach, *Proc. Phys. Soc.* B **66**, 386 (1953).
[8] Bowden and Tabor, "The Friction and Lubrication of Solids", Oxford University Press, 1950, p. 25.
[9] Bulgin, *Trans. Inst. Rubber Ind.* **21**, 188 (1945); Wack, Anthony, and Guth, *J. Applied Physics* **18**, 456 (1947).
[10] Mullins, *J. Rubber Research* **16**, 275 (1947).
[11] Schallamach, *J. Polymer Sci.* **9**, 385 (1952).
[12] Bowden and Tabor, "The Friction and Lubrication of Solids", Oxford University Press, 1950.

MIGRATION EFFECTS IN OVEN AGING *

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Oven aging tests on rubber compositions are known to be affected by other compositions with which they might be aged. The American Society for Testing Materials Method D573 recognizes this, and the procedure specifies that simultaneous aging of a mixed group of different compounds should be avoided if possible[1]. Few data exist in the literature on the extent of the effect of one material on another, although a recent paper[2] has presented data on this point for the oxygen-bomb method[3].

Aside from the effect on one material by another when aged simultaneously, there is also the possibility that ovens may become contaminated by continued use so that, even though simultaneous aging is avoided, an undesired effect may be produced.

This study was undertaken to determine the magnitude of these effects. As a part of this report, we also include some unreported data bearing on this subject which were obtained in a cooperative program sponsored by Section IV of the joint SAE-ASTM Committee on Automotive Rubber[4]. The authors are indebted to this committee for permission to use these data.

This latter program was undertaken to find the reason for the erratic behavior of a nitrile-rubber stock vulcanized with TMTD (tetramethylthiuram disulfide) in an earlier cooperative test program[5] designed to compare the test-tube method of aging with the oven method[6]. In this study, the oven-aging results obtained with this compound were unexpectedly erratic for those tests made at 70° and at 100° C. In the procedure used, it was specified that the aging tests at these two temperatures could be run simultaneously with the other compounds in the test program and concurrently with other routine aging tests. Tests at 125° and 150° C, however, were to be run individually. Since the 70° and 100° C oven tests for this material were the most erratic, a reasonable suspicion would be that this particular material was more sensitive to contamination by other materials than were the other stocks included in the program.

PROCEDURES

For most of the tests reported herein, the effects of one material on another were determined by the difference between the degradation observed for a single material aged by the test-tube method and that observed when the material was aged, also by the test-tube method, but with one dumbbell sandwiched between two dumbbells of the second stock and separated from them by about $\frac{1}{8}$ inch.

SAE–ASTM TESTS

For the cooperative SAE-ASTM program, aging tests were run, utilizing dumbbell specimens from the same lot of material as in the original tests.

* Reprinted from the *India Rubber World*, Vol. 128, No. 5, pages 623–625, August 1953.

Compound No. 2 was the nitrile-rubber stock referred to above, and Compound No. 3 was a natural rubber tread stock, normally compounded. Tests were run by the test-tube method with a dumbbell of Compound No. 2 sandwiched between two dumbbells of Compound No. 3. For each condition of exposure, three test tubes were prepared so that three specimens of Compound No. 2 would be available for testing. As controls, an additional tube containing three specimens of Compound No. 2 was run. Five laboratories participated in the tests. The times and temperatures chosen were as follows:

1024 hrs. at 70° C
128 hrs. at 100° C
24 hrs. at 125° C
4 hrs. at 150° C

TESTS BY GOODRICH RESEARCH CENTER

For the program conducted in the authors' laboratory, three natural-rubber tread-type compositions were chosen, having the formulations given below.

Compound	A	B	C
Natural rubber*	100	100	100
Zinc oxide	5	5	5
MBTS†	1	1	—
EPC black	50	50	50
Stearic acid	3	3	3
Sulfur	3	3	—
PBNA‡	—	1	1
TMTD	—	—	3.5

Cure 40 min. at 284° F

* A blend of smoked sheets was used.
† Benzothiazyl disulfide.
‡ Phenyl-β-naphthylamine.

Compound B is the natural-rubber tread-type recipe of ASTM Method D-15-52T. Standard pigments obtained from the Bureau of Standards were used except for the PBNA.

Special precautions were taken to prevent contamination of the stocks prior to the start of the aging tests. The mill rolls, guides, molds, and all tools were washed with acetone before and after each stock was processed. The operators washed their hands with soap and water before and after handling each stock. Both the unvulcanized stock and the cured sheets for a particular compound were kept isolated from the other compounds to prevent any migration of materials.

The first series of tests was run for the purpose of establishing that the deterioration by the test-tube method was equal to that obtained by the oven method when a new oven was used and that there was an appreciable difference in severity when an old oven was compared with a new oven. For these purposes, Compounds A, B, and C were aged as follows: (1) in test tubes in accordance with D865-50T; (2) individually in a new oven in accordance with D573-48; (3) individually in an oven which had been used for many years, also in accordance with D573-48.

Compound A was aged for 100 hours, and Compounds B and C for 1000 hours at 70° C. For both the aged and the unaged values of stress-strain, six specimens were tested.

For the second series of tests, Compounds A, B, and C were aged by the test-tube method at 70° C for various time intervals both alone and in various combinations as follows:

(1) Compound A aged alone, 50, 100, 200, and 400 hours.
(2) Compound B aged alone, 200, 400, 800, and 1600 hours.
(3) Compound C aged alone, 400, 800, 1600, and 3200 hours.
(4) Compound A aged between two specimens of Compound B and also between two specimens of Compound C for 50, 100, 200, and 400 hours.
(5) Compound B aged between two specimens of Compound A and also betwen two specimens of Compound C for 200, 400, 800, and 1600 hours.
(6) Compound C aged between two specimens of Compound A and also between two specimens of Compound B for 400, 800, 1600, and 3200 hours.

In each case a sufficient number of test tubes were aged at each interval so that six specimens of the compound of interest could be tested.

Separate mixes were made for the two series of tests which were run at different times. For this reason the results obtained in the two series are not strictly intercomparable.

In all cases the median values for tensile strength and modulus were determined.

RESULTS

For the cooperative test program, the pertinent data are given in Tables 1, 2, and 3. In Table 1 are given the averages for 300 per cent modulus, tensile strength, and elongation for the three specimens tested under each of the conditions chosen and for each of the five laboratories. The very marked differences between the two sets of data are evidence of a migration effect of some material originating in the conventional stock and affecting the TMTD cured nitrile rubber stock. It was observed that in all cases the specimens of Compound No. 2 sandwiched between specimens of Compound No. 3 developed a hard surface crust. As a matter of interest the average results previously reported[5] for these aging periods by the test-tube method are also shown. The agreement between the two sets of data is quite good.

The individual results from each laboratory for the oven-aged specimens of this same compound at 70 and 100° C, some of which were not included in the previous report[5], are shown in Table 2. It is evident that the degree of the migration effect varied widely from one laboratory to the next.

One laboratory in this test program reported stress-strain data on the specimens of Compound No. 3 between which the specimens of Compound No. 2 were sandwiched. A comparison of these results with the averages previously reported for the aging for the same times and temperatures should give an indication of the effect of Compound No. 2 on Compound No. 3. These data are given in Table 3 and show that in this case also an appreciable, though less radical, effect was found.

The results of the first series of tests run in the authors' laboratory are given in Table 4. These data show that the test-tube method and the oven method give results which are nearly identical when a new uncontaminated oven is used; but when an old oven is used, greater deterioration of all three stocks is observed.

The results of the second series of tests are given graphically in Figures 1 to 6 inclusive.

In Figures 1 and 2, Compound A is shown to deteriorate less for aging times of more than 100 hours when aged in close proximity to specimens of Compounds B and C.

TABLE 1

COMPOUND NO. 2 AGED BY TEST-TUBE METHOD

Time and temperature	Lab. No.	Aged alone: 300% modulus (lb. per sq. in.)	Aged alone: Tensile strength (lb. per sq. in.)	Aged alone: % elongation	Aged between two specimens of Compound No. 3†: Tensile strength (lb. per sq. in.)	Aged between two specimens of Compound No. 3†: % elongation
1024 hrs. at 70° C	1	1658	2658	483	633	83
	2	1883	2653	440	550	107
	3	*	2773	450	556	83
	4	1987	3050	453	663	100
	5	1769	2696	510	631	112
	Ave.	1824	2766	465	605	97
Ave. of previous tests		1861	2776	439		
128 hrs. at 100° C	1	1817	2658	460	600	123
	2	1793	2627	407	733	160
	3	*	2167	308	642	100
	4	2180	2723	393	823	156
	5	2095	2594	387	827	175
	Ave.	1971	2554	391	725	143
Ave. of previous tests		1863	2724	439		
24 hrs. at 125° C	1	1758	2558	450	912	200
	2	1950	2713	420	1063	213
	3	*	2537	516	741	168
	4	2150	2915	405	990	193
	5	2055	2656	400	1007	250
	Ave.	1978	2676	438	943	205
Ave. of previous tests		1819	2714	443		
4 hrs. at 150° C	1†	1575	2675	443	950	310
	2	1587	2583	460	1217	290
	3	*	2707	492	1037	233
	4	1730	2680	470	1173	250
	5	1645	2576	450	1127	275
	Ave.	1634	2644	463	1101	272
Ave. of previous tests		1475	2580	491		

* Modulus values not reported.
† Only one result was obtained for 300% modulus (lb. per sq. in.), which was 687, for Lab. No. 1—4hrs. at 150° C.

In Figures 3 and 4, Compound B is shown to be relatively unaffected by aging in close proximity to specimens of Compound A and Compound C.

In Figures 5 and 6, Compound C is shown to deteriorate very much faster when aged in close proximity to specimens of Compounds A and B than when aged alone.

TABLE 2

OVEN AGED RESULTS FOR COMPOUND NO. 2

Aging time and temperature	Lab. No.	300% modulus (lb. per sq. in.)	Tensile strength (lb. per sq. in.)	Elongation
1024 hrs. at 70° C	1	—	1800	275
	3	—	628	100
	5	2022	2515	420
128 hrs. at 100° C	1	—	1500	220
	3	—	966	172
	5	2076	2236	320
	6	1679	2548	448

TABLE 3

AGING DATA ON COMPOUND NO. 3

Aging time and temperature	Aged with Compound No. 2 Present data*		Aged alone previous data		
	Tensile strength (lb. per sq. in.)	Elongation (%)	300% modulus (lb. per sq. in.)	Tensile strength (lb. per sq. in.)	Elongation (%)
1024 hrs. at 70° C	1108	252	1635	1945	371
128 hrs. at 100° C	520	115	—	882	156
24 hrs. at 125° C	315	70	—	356	81
4 hrs. at 150° C*	690	343	620	864	370

* Only one result was obtained for 300% modulus (lb. per sq. in.), which was 572, for 4 hrs. at 150° C.

TABLE 4

COMPARISON BETWEEN TEST TUBE, NEW OVEN, AND OLD OVEN AT 70° C

	300% modulus	% retained	Tensile strength	% retained	Elongation	% retained
			Compound A			
Original	2250		3955		480	
100 hrs. in T. T.	1985	88.2	2895	73.2	420	87.4
New oven	1915	85	2780	70.3	425	88.5
Old oven	1765	78.3	2400	60.7	395	82.3
			Compound B			
Original	2440		4345		495	
1000 hrs. in T. T.	—		1410	32.3	230	46.5
New oven	—		1355	31	220	44.4
Old oven	—		1010	23.2	195	39.4
			Compound C			
Original	2010		3775		470	
1000 hrs. in T. T.	2305	114.8	3215	85.2	390	82.8
New oven	2340	116.3	3155	83.5	387	82.3
Old oven	2525	125.9	2875	76.2	335	71.2

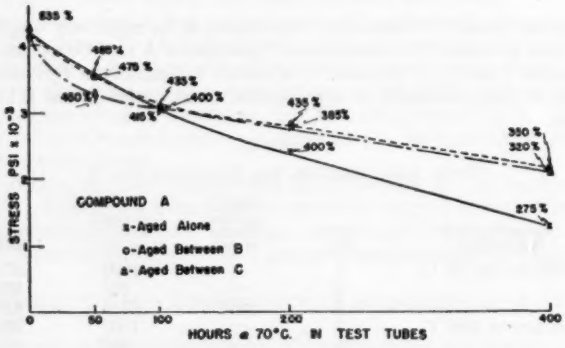

FIG. 1.—Tensile strength vs. aging time for Goodrich Compound A, alone and between Compounds B and C.

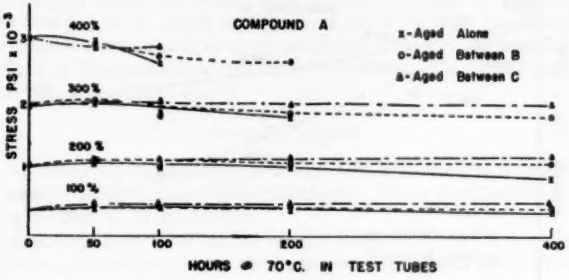

FIG. 2.—Modulus *vs.* aging time for Goodrich Compound A, alone and betaeen Compounds B and C.

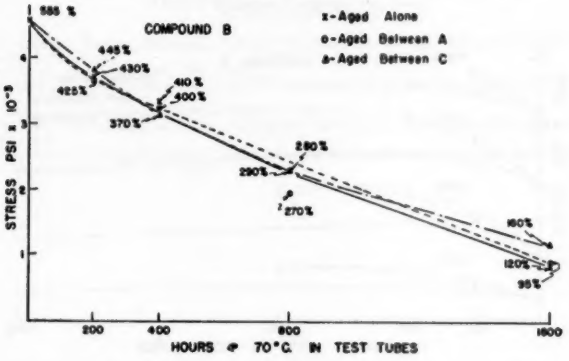

FIG. 3.—Tensile strength *vs.* aging time for Goodrich Compound B, alone and between Compounds A and C.

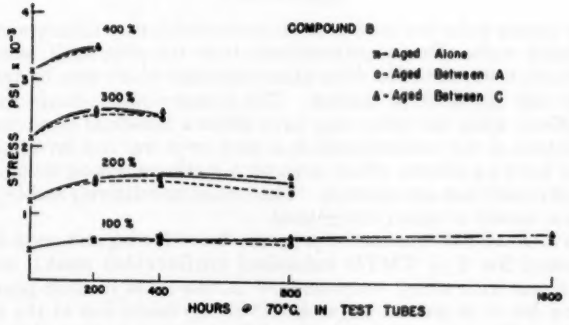

FIG. 4.—Modulus *vs.* aging time for Goodrich Compound B, alone and between Compounds A and C.

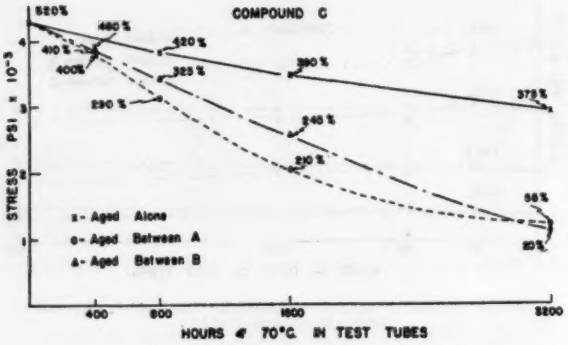

FIG. 5.—Tensile strength vs. aging time for Goodrich Compound C, alone and between Compounds A and B.

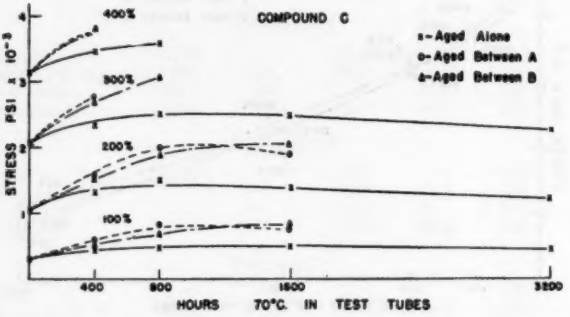

FIG. 6.—Modulus vs. aging time for Goodrich Compound C, alone and between Compounds A and B.

DISCUSSION

There appear to be two sources of materials which may influence the results of oven aging tests. One is contaminants from the oven itself, accumulated from previous tests; the other from other materials which may be aged simultaneously with the stock of interest. The former appear always to have an adverse effect; while the latter may have either a beneficial or adverse effect.

The nature of the contaminants in a used oven was not investigated, but since they have an adverse effect, even on a stock containing no age-resister, they are obviously not age-resisters. They could be relatively stable peroxides as well as a variety of sulfur compounds.

In the SAE-ASTM cooperative program, the stiffening and crust formation of Compound No. 2 (a TMTD vulcanized nitrile-rubber stock), when aged either in ovens with mixed compounds or in test-tubes in close proximity to Compound No. 3 (a normal sulfur stock) are no doubt due to the migration of sulfur or sulfur compounds capable of further cross-linking of the TMTD vulcanized stock.

The beneficial effect of Compounds B and C, both of which contained PBNA, on Compound A, which contained no age-resister in the Goodrich tests, is no doubt due to the migration of some of the PBNA to Compound A. The adverse effect of Compounds A and B on Compound C is similar to the case of Compound No. 2 discussed above.

CONCLUSIONS

Aging of materials individually in ovens contaminated from previous usage does not assure freedom from contamination. These contaminants cause an increase in the rate of deterioration.

Materials migrating from unlike stocks aged together may have varying effects, adverse, beneficial, or no effect, depending on the compositions being employed.

The test-tube method of aging is an excellent method for studying these migration effects as well as for conducting routine aging tests in their complete absence.

REFERENCES

[1] American Society for Testing Materials, "ASTM Standards for Rubber Products", ASTM Designation D573-48, Dec. 1952.
[2] Fackler and Rugg, *Anal. Chem.* **23**, 1646 (1941).
[3] American Society for Testing Materials, "ASTM Standards for Rubber Products", ASTM Designation D572-50, Dec. 1952.
[4] Society of Automotive Engineers, 29 West 29th St., New York, N. Y.
[5] Schoch and Juve, "Symposium on Aging of Synthetic Rubbers", ASTM Special Technical Publication No. 89 (1949).
[6] American Society for Testing Materials, "ASTM Standards for Rubber Products", ASTM Designations D573-48 and D865-50T, Dec. 1952.

CRACKING OF STRESSED RUBBER BY FREE RADICALS *

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The characteristic cracking of rubber by ozone has been well known for many years and has been the subject of numerous investigations. While this phenomenon has hitherto been considered unique with ozone, we find it not to be so, and that a cracking of rubber indistinguishable from that produced by ozone follows on exposure of stressed rubber to vapors of volatile peroxides irradiated by ultraviolet light. Moreover, the presence of oxygen is not necessary, the reaction occurring equally well in an atmosphere of nitrogen. Thus, the cracking apparently is due to the free radicals resulting from the photolysis of the peroxides. In the presence of nitrogen peroxide, the reaction is accelerated, as shown by an increase of the rate of rubber cracking and by a peroxide balance sheet, determined by chemical analysis. The photolyzed nitrogen peroxide evidently functions as a catalyst for the breakdown of the peroxide, since no change occurs in the dark. Cracking by such different radicals as tertiary-butoxy, phenyl, benzoyl, acetyl, and hydroxyl has been observed.

There have been frequent reports in the recent literature of unusually high concentrations of atmospheric ozone in the Los Angeles area, usually associated with "aerial smog". The identity of the ozone has been determined on the dual basis of liberation of iodine from potassium iodide solution and the cracking of stressed rubber. The high values are said to prevail only in the presence of sunlight and high concentrations of nitrogen oxides. In explanation[1], an interesting mechanism has been invoked, whereby nitrogen peroxide functions as a catalyst for ozone formation through the steps of photolysis by sunlight, with liberation of atomic oxygen and nitric oxide, formation of ozone by the former, and recombination of the latter with molecular oxygen to restore the nitrogen peroxide. A further suggestion involves the cooperation of peroxides or hydrocarbons susceptible to oxidation to volatile peroxides, ozone again being postulated as a final product.

In view of our laboratory observation of the cracking of rubber by free radicals, it appears to us that such a mechanism may be a contributing factor in rubber cracking under atmospheric conditions such as are present in the Los Angeles area, the radicals being produced by the catalyzed photolysis of volatile peroxides present in the smog.

Evaluation of the relative importance of this explanation, compared with the ozone mechanism, can be made only after sufficient data are available on ozone concentrations determined by positive means.

REFERENCES

[1] A. J. Haagen-Smit, *Ind. Eng. Chem.*, **44**, 1342 (1952); Second Technical and Administrative Report on Air Pollution Control in Los Angeles County.

* Reprinted from the *Journal of Polymer Science*, Vol. 11, No. 3, pages 280–281, September 1953.

AN INTERESTING PROPERTY OF CERTAIN CONDUCTIVE RUBBERS *

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During the course of electrical measurements of conductive rubbers, an interesting characteristic of some such materials was discovered. As far as we know, this characteristic has not been previously reported[1]. It was found that, under certain conditions, a polysulfide rubber (Thiokol LP_2)[2] shows a

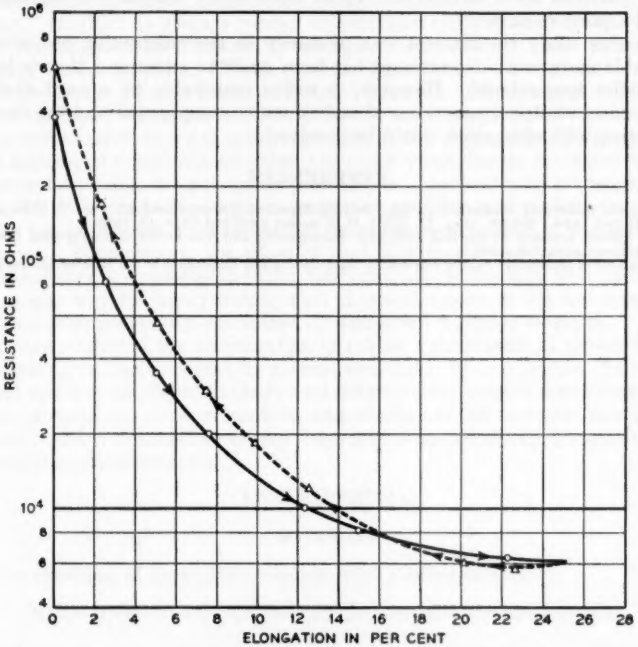

FIG. 1.—Example of negative resistance-elongation characteristics found in certain conductive rubbers.

decrease of electrical resistance as the material is stretched. The resistance declines up to elongations of perhaps 20 per cent. Beyond this it becomes fairly flat for an interval, and then increases from there on to the elastic limit. An example of elongation *vs.* resistance is shown by the full line of the accompanying figure.

* Reprinted from the *Journal of Polymer Science*, Vol. 10, No. 4, pages 447–448, April 1953.

There is also a "hysteresis" effect. That is, the variation of resistance with elongation follows a different relationship during extension than on return to normal. An example of the return-to-normal relationship is shown by the broken line in the accompanying figure.

Both the negative relationship of resistance to elongation and the hysteresis effect are apparently functions of a number of parameters. As we might expect, they change with curing procedure. Sheets from which early samples were taken were made by a spraying process. Heating and aging conditions were varied to determine, in a preliminary way, the importance of these effects. Both air-cured and milled heat-cured samples were measured. One general conclusion of these experiments is that the unique electrical characteristics are readily reproducible.

Other conductive elastic materials were measured. These included a conducting natural rubber[3], a Butyl material, and a Neoprene sample in which silver particles were embedded. In all these cases resistance-elongation followed a positive slope.

In this study the interest was primarily in the conductive properties of available materials. No attempt has been made to advance a theory for the properties encountered. However, it seems reasonable to suspect that the well-known electrical properties of carbon under compression and the decrease in section with elongation would be involved.

REFERENCES

[1] References concerning conductive rubbers include *Electrical Review* (London), June 3, 1938, p. 800; British patent 396,891 (Aug. 17, 1933); U. S. patent 2,466,963 (Apr. 12, 1949).

[2] R. C. Platow, formerly at the Bell Telephone Laboratories, and now at the U. S. Plywood Company, cooperated in this study.

[3] This sample of conductive rubber was kindly furnished by the Institution of the Rubber Industry.

STUDIES OF THE HEAT DETERIORATION OF SPECIALLY PREPARED NATURAL RUBBER VULCANIZATES *

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In 1949, Flory, Rabjohn, and Shaffer[1] presented an article describing the dependence of the elastic properties of vulcanized rubber on the degree of cross-linking. In order to prepare rubber vulcanizates characterized by known degrees of cross-linkage recently developed[2], disazodicarboxylate vulcanizing reagents were employed. These reagents react quantitatively with rubber, one cross-linkage being introduced for each molecule of the reagent. Whereas the conventional vulcanization of rubber with sulfur and accelerators is a complex process and it does not appear possible at the present time to specify the exact number of cross-linkages present in sulfur vulcanizates, the use of disazodicarboxylate vulcanizing reagents presents an opportunity to investigate the changes that occur in the physical properties of vulcanized rubber, characterized by known degrees of cross-linkage, on exposure to oxygen at elevated temperatures. Furthermore, the effect of heat deterioration of various chemical agents commonly employed in sulfur vulcanization recipes may be investigated in a unique way by incorporating such chemical agents in the free state into natural rubber previously vulcanized by disazodicarboxylate reagents.

Recent studies of the deterioration of rubber vulcanizates at elevated temperatures have been reported by several workers[3]. In this article, the experimental methods employed to study heat deterioration involve measurements of oxygen absorption, stress relaxation, and changes of 100 per cent modulus of natural rubber vulcanized to known extents of cross-linkage by decamethylenedismethyl azodicarboxylate.

EXPERIMENTAL

MATERIALS

The synthesis of decamethylenedismethyl azodicarboxylate:

$$CH_3O—CO—N=N—COO—(CH_2)_{10}—OOC—N=N—COOCH_3$$

and its behavior as a vulcanizing reagent is described[4] elsewhere. The purified product obtained by several recrystallizations from a mixture of equal volumes of ethyl acetate and hexane showed a constant melting point in the range 37.5–39° C. (This reagent will be referred to as DDMA throughout this article.) The DDMA was used immediately after preparation for the vulcanization of natural rubber.

Pale-crepe rubber was broken down slightly by repeated passes between mill rolls and then shredded. The rubber was then allowed to remain in contact with

* Reprinted from the *Journal of Polymer Science*, Vol. 11, No. 1, pages 83–92, July 1953.

TABLE I

CHEMICAL AGENTS STUDIED

1. Sulfur	6. Tetramethylthiuram disulfide (Tuads)
2. Phenylhydrazine	7. 2,2′-Mercaptobenzothiazole (Altax)
3. Cumene hydroperoxide	8. Diphenylguanidine (DPG)
4. Benzoyl peroxide	9. Di-*o*-tolylguanidine (DOTG)
5. Phenyl-β-naphthylamine (PBNA)	

acetone in darkness at room temperature for 36 hours. Following acetone extraction, the rubber was dried *in vacuo* at room temperature. A stock solution of the purified rubber containing about 5 per cent of rubber in benzene was prepared at room temperature, filtered under pressure and stored in darkness. The concentration of the stock solution was accurately determined by evaporating an aliquot portion to dryness and weighing the residue. The viscosity-average molecular weight of the rubber in the stock solution was found to be 870,000, using the constants of Carter, Scott, and Magat[5] to relate intrinsic viscosity in benzene with molecular weight.

Table I lists the various chemical agents employed in the present study. These materials were obtained from commercial sources and were used as received.

PREPARATION OF VULCANIZATES

Essentially the same procedure as that described by Flory, Rabjohn, and Shaffer[1] was used to prepare sheets of natural rubber vulcanized with DDMA. The thickness of the sheets ranged between 4 and 5 mils (inches $\times 10^3$). A total of four samples of natural rubber vulcanizate were prepared, containing the following equivalent percentages of DDMA: 0.20, 0.50, 1.00, and 1.50. Vulcanization with an equivalent percentage of 1.00 DDMA denotes, for example, that 1.00 per cent of the structural isoprene units are cross-linked (*i.e.*, 1 in every 100 isoprene units is cross-linked).

Samples of natural-rubber vulcanizates containing the different chemical agents listed in Table I were prepared in the following manner. A weighed sample of rubber[6] vulcanized with 1.00 per cent DDMA was allowed to swell in benzene at room temperature under nitrogen for 24 hours, after which time the weight of the swollen rubber was determined. Having specified the amount of benzene which enters into the rubber, it was then possible to calculate the quantity of chemical agent needed to be dissolved in benzene prior to swelling to yield a concentration of 3×10^{-4} (moles per gram of rubber) of chemical agent in the rubber vulcanizate. After the swelling operation, the rubber vulcanizate was dried to constant weight *in vacuo* at room temperature. From the increase of weight of the dried rubber, the amount of chemical agent incorporated into the rubber could be determined and the result was generally found to agree closely with the expected value.

APPARATUS

Oxygen absorption measurements were carried out at a constant oxygen pressure of 1 atmosphere in a static system. The apparatus employed has been previously described[7]. For the studies of continuous stress relaxation, a modified stress relaxometer[8] was used. The modification consisted of replacing the usual 100-gram rider for one measuring stresses up to 10 grams, and was necessitated because of the small loads required with rubber samples only 5 mils

thick. The measurements of continuous relaxation were made at 80° C and at 100 per cent elongation. This elongation was chosen, since it has been shown[1] that, at 100 per cent elongation, the stress in natural-rubber vulcanizate prepared with 1 equivalent per cent of DDMA agrees exactly with that expected from the rubber theory of elasticity. Actually, the deviation from theory is quite small for the rubber vulcanizates employed here, where the equivalent per cent of DDMA ranges from 0.20 to 1.50.

The change in 100 per cent modulus of the rubber vulcanizates during exposure at air at 80° C was measured with the stress relaxometer under the conditions usually employed for intermittent stress relaxation measurements[9].

Creep measurements of the rubber sample containing 1 equivalent per cent of DDMA at 80 and 100° C were made in an apparatus of the type previously described[10]. The entire unit, however, was considerably reduced in size and could be inserted into a wide (80 mm.) glass tube. The entire system could then be evacuated to 10^{-4} mm. Hg.

EXPERIMENTAL RESULTS

DEPENDENCE OF HEAT DETERIORATION ON EXTENT OF VULCANIZATION

In Figure 1 are represented the changes of 100 per cent modulus at 80° C of the four natural-rubber vulcanizate samples prepared with 0.2, 0.5, 1, and 1.5 equivalent per cent of DDMA. In Figure 2 the relative rates of continuous

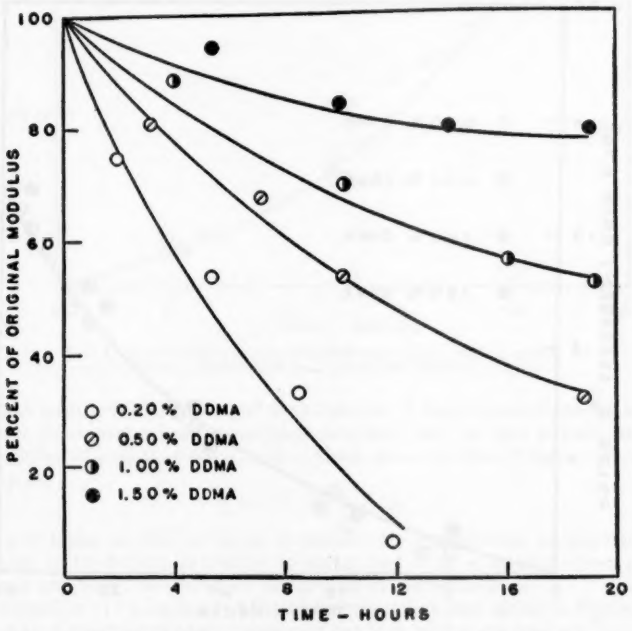

FIG. 1.—Changes in 100 per cent modulus of natural rubber vulcanized to various extents with decamethylenedismethyl azodicarboxylate (DDMA) at 80° C.

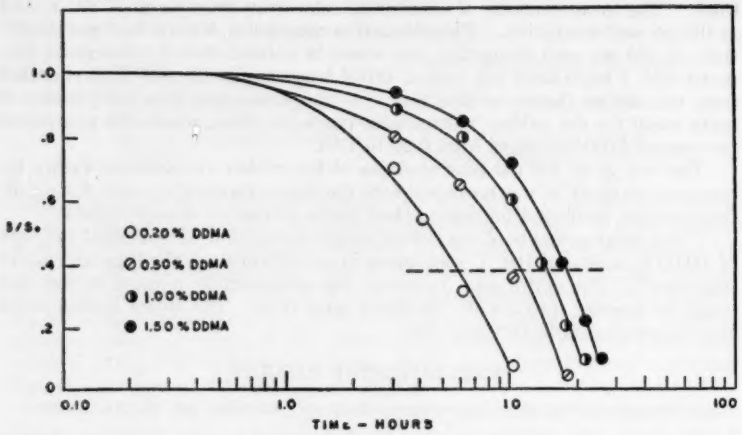

FIG. 2.—Relaxation in stress of natural rubber vulcanized to various extents with decamethylenedimethyl azodicarboxylate (DDMA) at 80° C and 100 per cent elongation.

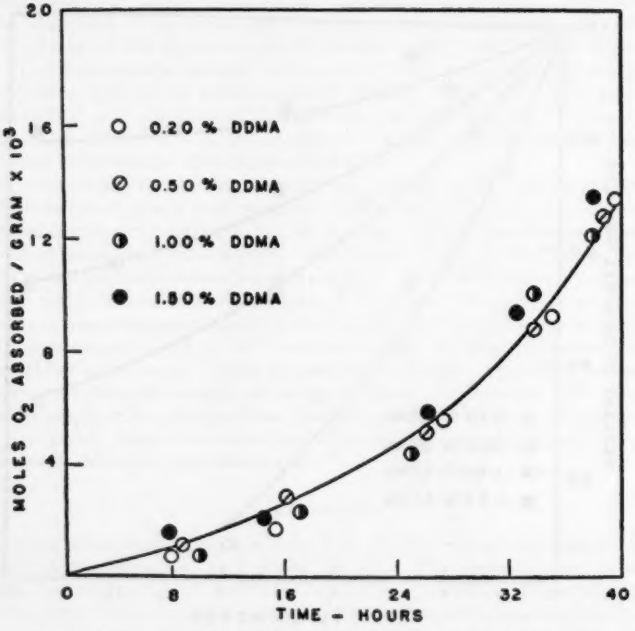

FIG. 3.—Oxygen absorption of natural rubber vulcanized to various extents with decamethylenedimethyl azodicarboxylate (DDMA) at 80° C.

stress relaxation of these same four samples at 80° C are shown. In this figure, the stress divided by initial stress (S/S_0) is plotted as a function of logarithmic time. The horizontal dotted line in Figure 2 indicates the point at which the relative stress has decayed to $1/eth$ (0.38) of the original stress. It would seem from Figures 1 and 2 that the higher the amount of DDMA in the rubber vulcanizate, the more resistant the rubber becomes to heat deterioration. On the other hand, it is evident from Figure 3 that the rates at which these four rubber samples undergo oxidation at 80° C are nearly identical. In this case, the moles of oxygen absorbed per gram of rubber are plotted as a function of time.

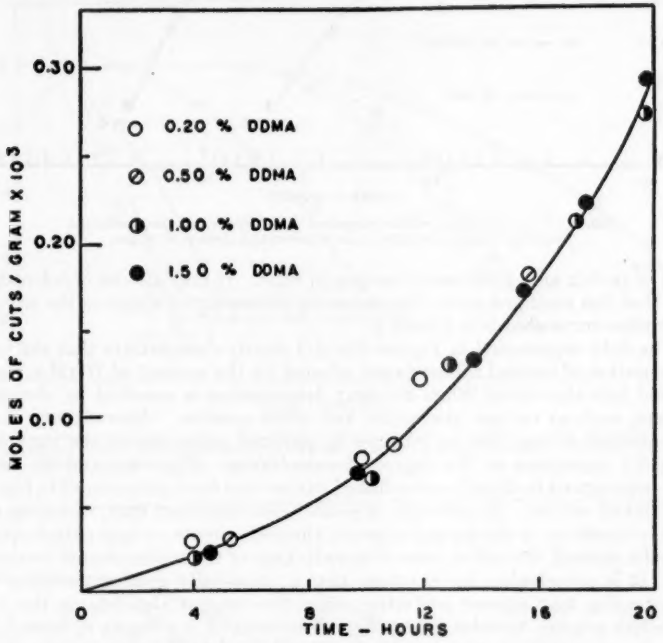

FIG. 4.—Chain scission in natural rubber vulcanized to various extents with decamethylenedismethyl azodicarboxylate (DDMA) at 80° C.

It has been previously shown[11] that the rate of continuous stress relaxation of rubber vulcanizates held at constant extension may be used to calculate the total number of cuts that occur in the rubber as a function of time. The relationship is:

$$q = -1/M_c \ln S/S_0 \qquad (1)$$

where q = moles of cuts per gram of rubber, M_c = molecular weight between cross-links of the vulcanizate prior to aging, and S/S_0 = relative stress of the rubber at any time, measured by continuous stress relaxation.

If Equation (1) is applied to the stress relaxation data given in Figure 2, it is found that the rates of chain scission of the four rubber samples are identical. These calculations are represented in Figure 4, where the moles of "cuts" per

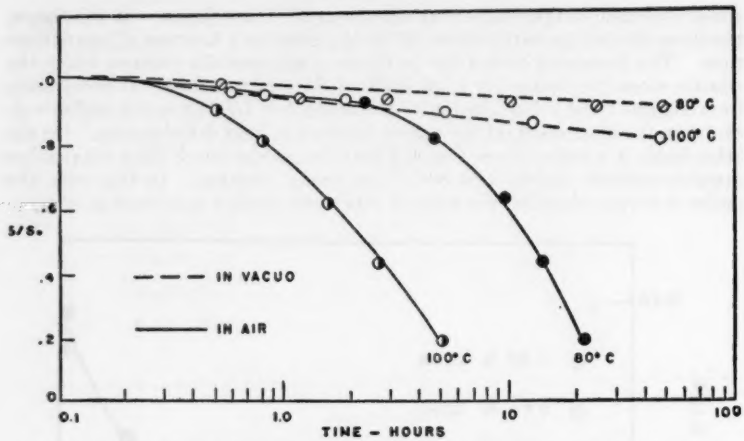

FIG. 5.—Creep of natural rubber vulcanized with 1.00 per cent decamethylene-diamethyl azodicarboxylate in the presence and absence of oxygen.

gram of rubber are plotted as a function of time. It may also be of interest to note that the resultant curve has the same autocatalytic shape as the oxygen absorption curve shown in Figure 3.

The data represented in Figures 3 and 4 clearly demonstrate that the heat deterioration of natural rubber is not affected by the amount of DDMA incorporated into the rubber when the heat deterioration is specified by chemical changes, such as oxygen absorption and chain scission. Alternatively, heat deterioration as specified by changes in physical properties of the rubber is markedly dependent on the degree of cross-linkage (Figures 1 and 2), being most pronounced in slightly cross-linked rubber and least pronounced in highly cross-linked rubber. In principle, it would seem important that, whenever the relative beneficial or deleterious action of chemical agents on heat deterioration are to be studied, the initial state of cross-linkage of the rubber should be specified. It is conceivable, for example, that a potentially good antioxidant for rubber aging may appear ineffective, since the reagent also retards the vulcanization process, thereby producing vulcanizates of low degree of cross-linkage. In any event a comprehensive study of heat deterioration might well include observations of chemical changes as well as changes in physical properties.

It is possible that the heat deterioration of the rubber samples vulcanized with DDMA arises from causes other than oxidative breakdown. The DDMA reagent, for example, might contain weak linkages, which decompose thermally at that temperature (80° C) used in this study. To explore this possibility further, studies were made of the creep behavior of the vulcanizate prepared with 1 equivalent per cent of DDMA at 80° and 100° C in the presence and absence of oxygen. The results obtained are given in Figure 5, where it is seen that, in the absence of air, the rate of creep is almost negligible relative to the rate when oxygen is present. The creep function (S/S_0) is plotted against logarithmic time in the same manner as continuous stress relaxation data. The relationship between creep and stress relaxation measurements in terms of the scission and cross-linking processes that accompany the heat deterioration of rubber have been discussed[10] previously. In this instance, creep rather than

stress relaxation was employed for reasons of experimental simplicity. Stress relaxation measurements in the absence of air require an elaborate apparatus[12], while creep measurements *in vacuo* are relatively simple to perform.

EFFECT OF CHEMICAL AGENTS ON HEAT DETERIORATION

Studies of the relative rates of stress relaxation of natural-rubber vulcanizate containing the various chemical agents listed in Table I are shown in Figures 6 and 7. The studies were made at 80° C, using a rubber vulcanizate

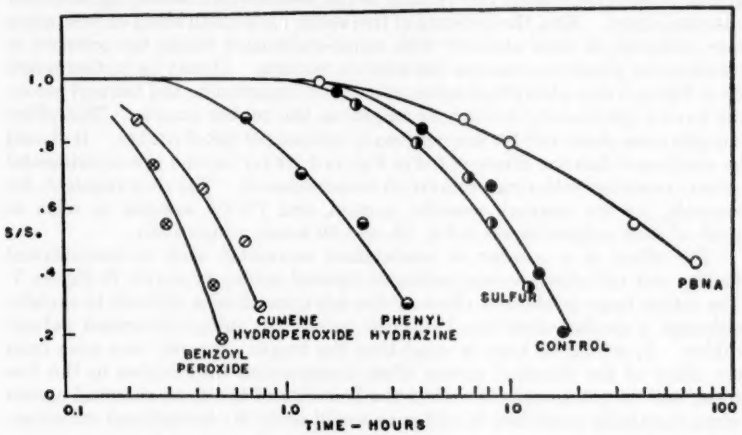

FIG. 6.—Effect of chemical agents on continuous stress relaxation of natural rubber vulcanized with 1.00 per cent decamethylenedismethyl azodicarboxylate at 80° C and 100 per cent elongation. Concentration of chemical agents = 3×10^{-4} mole per gram rubber.

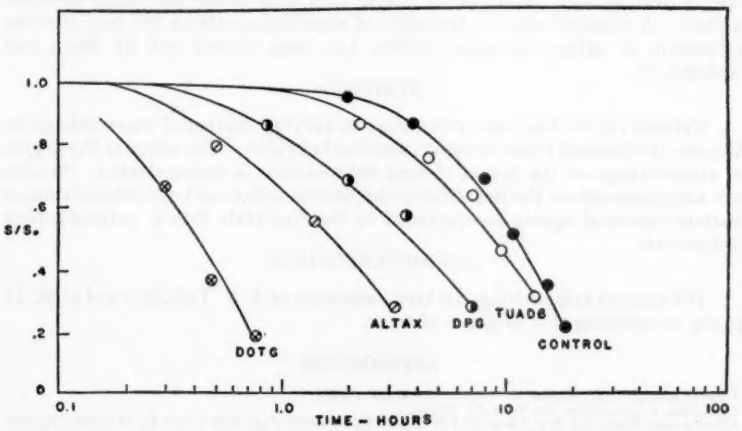

FIG. 7.—Effect of chemical agents on continuous stress relaxation of natural rubber vulcanized with 1.00 per cent decamethylenedismethyl azodicarboxylate at 80° C and 100% elongation. Concentration of chemical agents = 3×10^{-4} mole per gram rubber.

prepared with 1 equivalent per cent of DDMA. This amount of DDMA corresponds to a vulcanizate having an average molecular weight between cross-links of 6,800, *i.e.*, $M_c = 100 \times$ molecular weight of each isoprene residue. As previously mentioned, the chemical agents were incorporated in the free state into the rubber vulcanizate by swelling the rubber in benzene containing an appropriate amount of the chemical agent. Inasmuch as the initial extent of cross-linkage of each rubber sample was the same, the only apparent way in which the samples could exhibit differences in relaxation rate is by the influence of the added chemical agent. As seen in Figure 6, the antioxidant, PBNA, greatly retards the scission rate relative to the control stock containing no added chemical agent. Also, the presence of free sulfur has a small effect on relaxation rate, although in other studies[13] with sulfur-vulcanized stocks the presence of excess sulfur greatly accelerates the scission reaction. It may be further noted from Figure 6 that phenylhydrazine, cumene hydroperoxide, and benzoyl peroxide have a particularly deleterious action on the rubber sample. This effect has also been observed[14] for conventionally vulcanized GR-S rubber. It should be mentioned that the effects noted in Figure 6 are far beyond the experimental errors associated with stress-relaxation measurements. The time required, for example, for the benzoyl peroxide, control, and PBNA samples to relax to $1/e^{th}$ of their original stress is 0.4, 13, and 99 hours, respectively.

The effect of a number of accelerators commonly used in conventional (sulfur and sulfurless) vulcanization of natural rubber is shown in Figure 7. The rather large deleterious effect of di-*o*-tolylguanidine is difficult to explain, although a similar effect has also been noted[13] for sulfur-vulcanized natural rubber. It should be kept in mind that the results observed here arise from the effect of the chemical agents when incorporated into rubber in the free state, and do not necessarily reflect the behavior of the same chemical agents when chemically combined in rubber as would occur in conventional vulcanization.

A wide variety of other chemical agents might also be studied. However, it is the purpose of this article to discuss the aforementioned technique for specification of heat deterioration rather than to evaluate the many chemical agents. A detailed study of the effect of chemical agents on the rate of stress relaxation of sulfur-vulcanized rubber has been carried out by Stern and Tobolsky[13].

SYNOPSIS

Natural rubber has been vulcanized to varying degrees of cross-linkage by the use of decamethylenedismethyl azodicarboxylate. The effect of the degree of cross-linkage on the extent of heat deterioration is demonstrated. Studies are also presented on the beneficial or deleterious action on heat deterioration of various chemical agents incorporated in the free state into a natural-rubber vulcanizate.

ACKNOWLEDGMENT

The authors acknowledge the kind assistance of A. V. Tobolsky and of M. D. Stern in outlining this program of work.

REFERENCES

[1] Flory, Rabjohn, and Shaffer, *J. Polymer Sci.* **4**, 225 (1949).
[2] Rabjohn, *J. Am. Chem. Soc.* **70**, 1181 (1948).
[3] Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944); Scott, *Trans. Inst. Rubber Ind.* **21**, 78 (1945); Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947); Cole and Field, *Ind. Eng. Chem.* **39**, 174 (1947); Throdahl, *Ind. Eng. Chem.* **40**, 2180 (1948); Mesrobian and Tobolsky, *Ind. Eng. Chem.* **41**, 1496 (1949).

[4] Rabjohn, *J. Am. Chem. Soc.* **70**, 1181 (1948); Flory, Rabjohn, and Shaffer, *J. Polymer Sci.* **4**, 225 (1949).
[5] Carter, Scott, and Magat, *J. Am. Chem. Soc.* **68**, 1480 (1946).
[6] The rubber vulcanizate containing 1 equivalent per cent of DDMA was used, since it has been shown[1] that, at this extent of cross-linkage, there is little change of the stress of the vulcanizate at 100 per cent elongation before and after swelling.
[7] Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947).
[8] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944); Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945).
[9] Tobolsky, Prettyman, and Dillon, *J. Applied Physics* **15**, 380 (1944); Tobolsky and Andrews, *J. Chem. Physics* **13**, 3 (1945); Mesrobian and Tobolsky, *J. Polymer Sci.* **2**, 463 (1947); *Ind. Eng. Chem.* **41** 1496 (1949).
[10] Andrews, Mesrobian, and Tobolsky, *Trans. Am. Soc. Mech. Engrs.* **67**, 569 (1947).
[11] Tobolsky, Mets, and Mesrobian, *J. Am. Chem. Soc.* **72**, 1942 (1950).
[12] Andrews, Hanson, and Tobolsky, *J. Applied Physics* **17**, 352 (1946).
[13] Stern, M. D., Ph.D. Thesis, submitted to the Chemistry Department, Princeton University, June 1948.
[14] Mesrobian and Tobolsky, *Ind. Eng. Chem.* **41**, 1496 (1949).

EFFECT OF THE CONCENTRATION AND NATURE OF THE EMULSIFYING AGENT ON THE STATE OF DISPERSION OF LATEXES *

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Yurzhenko and Mintz were the first to show that, in the process of emulsion polymerization, the size of the polymeric particles in the latex increases regularly[1]. This phenomenon is in complete accord with the theory that, in the particular case of 1,3-butadiene, polymerization proceeds to a major extent in the micelles of the emulsifying agent.

A systematic study of the state of dispersion of synthetic latexes in its relation to the experimental conditions and the processes taking place during their formation would appear to be of great potential value in the study of the mechanism of emulsion polymerization.

The present authors have studied the degree of dispersion of synthetic latexes prepared in the laboratory, with different concentrations and types of emulsifying agents. Work in this field has not been reported in the scientific literature, although, in studies of emulsion polymerization, data on the state of dispersion of latexes under certain conditions have been reported[2].

In the present work, the effects of other factors, such as the nature of the monomer, initiator, and electrolytes, on the size of the latex particles and the characteristics of these particles also were studied.

The state of dispersion of synthetic latexes in the colloid range was determined by measuring the turbidity: $\tau = I_p/I_0$, where I_p is the intensity of scattered light, and I_0 the intensity of light which passes through the solution. The turbidity was measured with a nephelometric attachment to a Pulfrich photometer at the wave length 5300 A. The dispersion of various latexes was estimated by the slope of a line which expresses the linear relation of the turbidity τ to the concentration c of the polymer at high dilutions (up to 1:5000, 1:10,000). Comparisons of the turbidities of dilute latexes were made at identical concentrations of polymer in the latexes. The radius of the polymeric particles was calculated by Rayleigh's or Debye's equation[3]. The possibility of using the light-scattering method for studying the state of dispersion of synthetic latexes had been considered earlier by the authors[4].

Styrene and isoprene latexes were prepared in sealed glass ampoules (dilatometers) under the following conditions: the phase ratio was 1:5; the degree of polymerization S for styrene latexes was near 100 per cent and for isoprene 50 per cent: the polymerization temperature was 45° C for styrene and 65° C for isoprene; the initiator was 0.005 M potassium persulfate for the water phase and 0.5 per cent phenyldimethylcarbinol hydroperoxide for the monomer. The emulsifiers used were carefully purified sodium dibutyl benzenesulfonate (DBBSK), sodium eicosylbenzenesulfonate (Sulfanol), sodium dibutyl-1-

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naphthalenesulfonate (Nekal), and sodium oleate, the micellar weight, conjugate solubility, and other properties of which had been studied in detail[5].

EXPERIMENTAL DATA

Effect of concentration of emulsifying agent.—Results of measurements of the light-scattering of isoprene and styrene latexes are shown in Figure 1 and Table 1. From these data it follows that, with decrease of the concentration of the emulsifier, the size of the particles in a latex increases, and that this regularity rule is independent of the nature of the initiator used.

The increase of the size of the latex particles with decrease of the concentration of the emulsifier can be explained by the fact that, with decrease of the concentration of the micellar centers of polymerization for a given quantity of

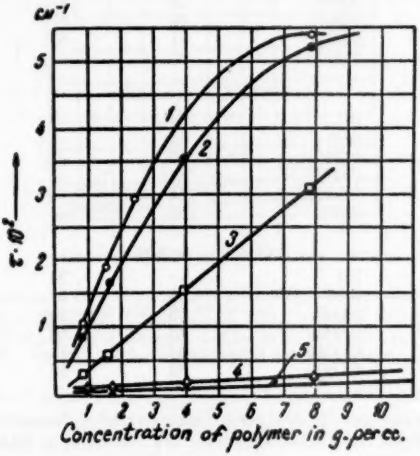

FIG. 1.—Effect of the concentration on the state of dispersion of polyisoprene latexes, with potassium persulfate as initiator. Curve 1. Concentration of emulsifying agent 0.0006 *M*. Size of polymeric particles 63 mμ. S 30 per cent. Curve 2. Concentration of emulsifying agent 0.00125 *M*. Size of polymeric particles 58 mμ. S 58.8 per cent. Curve 3. Concentration of emulsifying agent 0.005 *M*. Size of polymeric particles 44 mμ. S 60.6 per cent. Curve 4. Concentration of emulsifying agent 0.05 *M*. Size of polymeric particles 19 mμ. S 61 per cent. Curve 5. Concentration of emulsifying agent 0.1 *M*. Size of polymeric particles —. S 61 per cent.

monomer, the proportion of the latter in the micelles increases. There is a particularly sharp increase of size of the polymeric particles when the concentration of emulsifier falls below the critical concentration of micelle formation, that is, when hardly any micelles are present, and, therefore, when hardly any monomer is in colloid solution. The maximum particle size is attained when polymerization is carried out in the absence of an emulsifying agent. In this case, polymerization proceeds within the droplets and takes place very slowly.

If one assumes that the essential part of the polymerization process takes place in the micelles and that their concentration is proportional to the total concentration of emulsifier c, then it is evident that this concentration must be related to the radius of the latex particles r:

$$c_1 : c_2 = r_2^3 : r_1^3 \quad \text{or} \quad r_2 = Kc_2^{-\frac{1}{3}}$$

where $K = r_1 c_1^{\frac{1}{3}}$.

TABLE 1

EFFECT OF THE CONCENTRATION AND NATURE OF THE EMULSIFIER ON THE STATE OF DISPERSION OF SYNTHETIC LATEXES

(Size of polymeric particles in mμ)

No. p/p	Concentration of emulsifier in moles per l.	Styrene		Isoprene
		Potassium persulfate	Dimethylphenylcarbinol hydroperoxide	Potassium persulfate
		Nekal as emulsifier		
1	0.1	24	24	17
2	0.05	28	26	19
3	0.02	38	—	—
4	0.005	59	47	44
5	0.0025	83	67	47
6	0.00125	91	83	58
7	0.0006	95	—	61
		DBBSK as emulsifier		
1	0.1	24	—	29
2	0.05	34	—	31
3	0.005	50	—	35
4	0.0025	64	—	39
5	0.00125	71	—	47
6	0.006	100	—	63
		Sulfanol as emulsifier		
1	0.1	—	24	20
2	0.05	35	30	28
3	0.005	39	40	30
4	0.0025	49	58	33
5	0.00125	68	71	35
6	0.0006	82	84	40

Values of the radius of polystyrene latex particles, found experimentally and also calculated from the above equation, are recorded in Table 2. The value of K was found from the value of r_1 for a concentration of emulsifier equal to 0.005 M.

Sharp divergencies between the calculated values and those obtained experimentally for the radius are observed for concentrations of emulsifying agent lower than the critical values, *i.e.*, when the emulsifier is present in molecular form and not in micellar form in the aqueous phase.

TABLE 2

CALCULATED AND DETERMINED EXPERIMENTALLY, RADII OF LATEX PARTICLES (IN Mμ)

Concentration of emulsifier (mole per l.)	Nekal		Sodium oleate	
	r (experimental)	r (calculated)	r (experimental)	r (calculated)
0.1	24	22	23	15
0.05	28	26	25	19
0.02	38	37	—	—
0.005	59	59	41	41
0.0025	83	72	49	52
0.00125	91	93	68	65

Effect of the nature of the emulsifying agent.—The influence of the nature of the emulsifier is evident by the state of dispersion of the latexes. Here it is necessary to distinguish three cases.

(1) *When the concentration of emulsifying agent is greater than the critical value.*—In this case the state of dispersion of the latex is governed by the state of dispersion (micellar weight) of the emulsifying agent. For the emulsifying agents studied, the following micellar weights were obtained[5]: Nekal 33,300, DBBSK 91,000, Sulfanol 161,000. The state of dispersion of latexes is indicated in Figure 2.

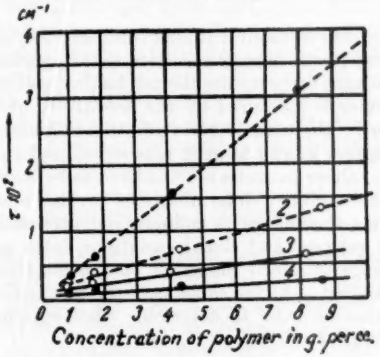

FIG. 2.—Effect of the nature of the emulsifying agent on the state of dispersion of polyisoprene latexes, with potassium persulfate as initiator and with 8 58–62 per cent. Curve 1. Nekal, size of polymeric particles 44 mμ. Curve 2. Sulfanol, size of polymeric particles 35 mμ. Curve 3. Sulfanol, size of polymeric particles 28 mμ. Curve 4. Nekal, size of polymeric particles 19 mμ. Curves 1 and 2. Concentration of emulsifying agent 0.005 *M*. Curves 3 and 4. Concentration of emulsifying agent 0.05 *M*.

(2) *In the range of critical concentrations.*—Latexes of high states of dispersion are formed with emulsifying agents whose critical concentrations are relatively low (Sulfanol in Figure 2).

(3) *When the concentration of the emulsifying agent is lower than the critical value.*—This range was studied by the authors.

In all cases, it is necessary to take into account the concentration of emulsifier in the gaseous phase of the emulsion after the formation of the adsorption layers on the phase boundary.

REFERENCES

[1] Yurzhenko and Mintz, *Doklady Akad. Nauk SSSR* **65**, 339 (1947).
[2] Hauser and Perry, *J. Phys. & Colloid Chem.* **7**, 1175 (1948); Tkachenko and Khomikovskiĭ, *Doklady Akad. Nauk SSSR* **72**, 543 (1950); Harkins, *J. Polymer Sci.* **2**, 287 (1950).
[3] Debye, *J. Phys. & Colloid Chem.* **5**, 18 (1947).
[4] Yurzhenko and Gusyakov, *Kolloid. Zhur.* **14**, 141 (1952).
[5] Yurzhenko and Kucher, *Kolloid. Zhur.* **13**, 226 (1951); *Doklady Akad. Nauk SSSR* **75**, No. 6 (1952).

ELECTROPHORETIC MOBILITY STUDY OF FRESH HEVEA LATEX *

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To both the producer of natural rubber latex and the manufacturer of latex goods, the stability of Hevea latex is one of its most important properties. Two aspects of this important property are the mechanical stability and the chemical stability. The former is measured by the sensitivity of latex to mechanical agitation, the latter by the sensitivity to addition of ionic material. Although there is no clear relation known to exist between these two stabilities, the electrical charge on the rubber particles is considered to be important in either case. Since electrophoretic mobility determinations furnish one of the most direct methods for studying the charge on colloidal particles such as those in rubber latex, the effect of seasonal and clonal variations, latex aging, ionic strength, pH, and the presence of added materials on the electrical mobility of fresh Hevea latex was studied. At the same time the mechanical stability of many latexes was measured in order to determine what correlation exists between mobility and mechanical stability.

EXPERIMENTAL WORK

The micromethod described by Abramson, Moyer, and Gorin[1] was used to study the mobility of latex.

A flat, horizontal, glass microelectrophoresis cell of the Briggs type[2] was used, with a mercuric nitrate solution in the lower part of the electrode compartment and half-saturated potassium nitrate in the upper. The cell width was 23.6 mm. and depth 0.785 mm., giving a width-to-depth ratio of 30. The glass cell was mounted on a metal frame which rested on the microscope stage. A 20× Spencer objective and a 20× Bausch and Lomb ocular provided a magnification of 400×. The fine adjustment scale of the microscope was calibrated by means of a slide of known thickness. An eyepiece micrometer, calibrated with a stage micrometer, was used to measure the velocity of the moving particles. For measuring the conductivity of the dispersions, a conductivity bridge[3] was used, along with a dip-type cell having a cell constant of 0.916.

A series of velocity measurements was made on one dispersion at various depths in the glass cell. The best parabola was drawn through the points of the velocity-depth plot, and the resulting curve was integrated graphically. The true electrophoretic velocity was thus found to occur at the 0.20 and 0.80 fractional depth levels. The theory of Komagata[4] predicts values of 0.205 and 0.795 for a cell whose width-to-depth ratio is 30. All velocity measurements were, therefore, made by averaging the values measured at the 0.20 and 0.80 levels. pH was measured with a glass electrode assembly[5]. Room temperature varied between 28.5° and 32.5° C during the course of all experiments, and the

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temperature of each dispersion was maintained at 30.0° ± 1.0° C while measurements were being made.

All mobility measurements except those after various aging periods were made by allowing approximately 3 cc. of latex to flow directly from the tapping cut of the tree being studied into 500 cc. of boiled distilled water 5 minutes after the flow of latex had started. The dilute suspension thus obtained was then taken immediately to the laboratory, where dispersions in buffer solutions of the desired concentrations and pH values were made. The mobility measurements were then made immediately on these dispersions, and the conductivity and pH measurements were all completed on the same day the latex was obtained. An acetate buffer was used in the pH range 3 to 6, although it was difficult to obtain satisfactory results at pH values above 5.5 with this buffer. At pH values above 6.0, a disodium hydrogen phosphate buffer was used, with the appropriate quantity of hydrochloric acid or sodium hydroxide added to reach the desired pH. The ionic strength of all buffer solutions was 0.02, except in one series of experiments in which the effect of ionic strength on mobility was studied. All mechanical stability determinations were made at a total solids concentration of 51.5 per cent.

RESULTS AND DISCUSSION

Dry Rubber Content.—The first variable investigated was the dry rubber content of the dispersions. The dry rubber content of the original dilute dispersion obtained by allowing the latex to fall into distilled water was determined, and that of the final dispersion in buffer solution was calculated from this determination. At dry rubber contents of over 1.0 gram per liter, it was difficult to pick out and follow one individual particle in the microscope field. At higher dilutions, on the other hand, there is danger that material will be desorbed from the surface of the particle, changing the surface characteristics. In Figure 1 the mobility is plotted as a function of dry rubber content for two different trees, one a seedling tree and the other a War. 4 clonal tree. The mobility is seen to decrease rapidly below concentrations of 0.5 gram per liter of rubber, and all subsequent measurements were made at dry rubber concentrations between 0.5 and 1.0 gram per liter.

Clonal Variation.—The variation of mobility with pH was determined for a series of clonal trees and for one seedling tree. In all cases the curves were typical of those for proteins, the only important difference from tree to tree being a slight displacement in the curve along the pH axis. Such a displacement results in a different isoelectric point, determined by the intersection of the best curve through the experimental points with the zero mobility line. The isoelectric points for several clones are shown in Table I, and a typical plot of mobility against pH is shown in Figure 2.

Carried out under tropical conditions, the microelectrophoresis method should be sufficiently accurate to determine the isoelectric point within 0.1 pH unit. The data of Table I show that there is considerable variation of the isoelectric point from clone to clone, a small but definite variation from tree to tree within one clone, and probably a very small daily variation for one tree. All the isolectric point values are grouped around 4.3 except those for the first War. 4 tree, which are higher, and those for the Av. 152 trees and the seedling tree, which are lower. Moyer[6] has found that closely related species of Euphorbia are marked by similar latex electrophoretic properties. The results presented in Table I show that among these even more closely related varieties of Hevea

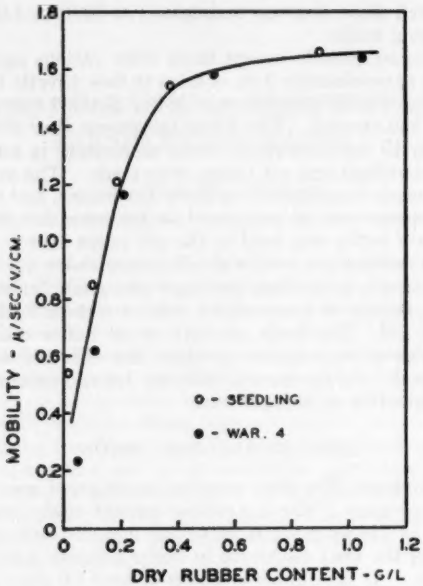

FIG. 1.—Effect of dry rubber content on mobility.

Buffer ionic strength 0.02
pH 5.4 to 5.5

brasiliensis there are small but measurable differences in the nature of the latex particle surface. These differences are reflected in mechanical stability determinations only after a definite aging period of the latex in the presence of a preservative such as ammonia[7].

Seasonal Variation.—In Figure 3 there is shown the variation of mobility with pH for a P.B. 186 tree. The circles represent the experimental points determined on February 12, 1950, when the tree was completely defoliated, and the squares those determined on April 13, 1950, when the new leaves were nearly

TABLE I

ISOELECTRIC POINT OF LATEXES FROM INDIVIDUAL TREES
(Alternate daily tapping, September–December 1950)

Tree no.	Clone	Isoelectric point[a]
1	War. 4	4.50, 4.62
2	War. 4	4.36, 4.36
3	P.B. 186	4.39, 4.31
4	P.B. 186	4.23, 4.25
5	Av. 50	4.30
6	B.D. 10	4.30
7	Av. 152	4.17
8	Av. 152	4.04
9	Seedling	4.24, 4.20, 4.08

[a] Duplicate or triplicate results on one tree represent separate determinations made on latex from that tree collected on different days.

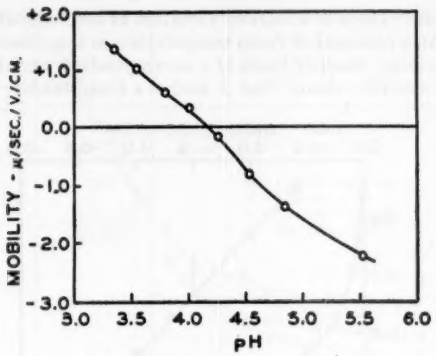

FIG. 2.—Effect of pH on mobility.

Buffer ionic strength 0.02
Av. 152 latex

completely grown. Any slight differences is within experimental error. If physiological changes taking place in the tree during wintering affect the nature of the rubber particle surface, such changes are not revealed in these mobility experiments.

Ionic Strength.—The effect of buffer ionic strength on the mobility of a P.B. 186 latex is shown in Figure 4, where mobility is plotted against ionic strength on the lower scale and the logarithm of the ionic strength on the upper scale. These determinations were made with disodium hydrogen phosphate buffers, whose pH values varied from 9.0 to 9.4. The latex dispersions were prepared from 62 per cent total solids centrifuge concentrate which had aged 90 days in the presence of 0.7 per cent ammonia. With the most dilute buffer, the mobility is very high, nearly 7.0 microns/second/volt/cm. The addition of ionic material decreases the mobility very sharply at first, then less rapidly at higher ionic strengths, following a logarithmic relationship very closely.

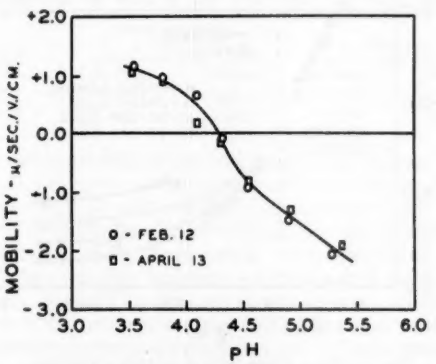

FIG. 3.—Effect of wintering season on mobility-pH relation of latex.
Buffer ionic strength 0.02

Aging of Latex.—There is a marked variation in mechanical stability among clonal latexes which are aged at room temperature in the presence of ammonia. In order to determine whether there is a corresponding variation in mobility, samples of a low stability clone, War. 4, and of a high stability clone, P.B. 186,

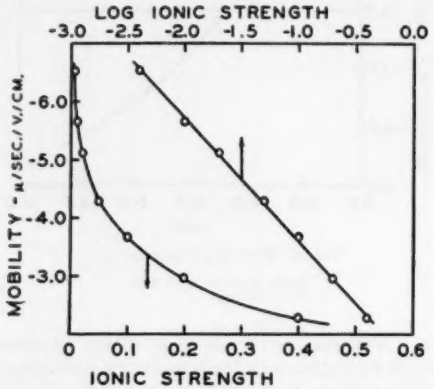

FIG. 4.—Effect of buffer ionic strength on mobility.
pH 9.0 to 9.4

were obtained and mobilities were measured immediately on the concentrates produced from these samples on a laboratory centrifuge. Mobilities were also determined upon these concentrates after aging periods of 30 and 90 days at 62 per cent total solids and 0.7 per cent ammonia (based on total latex). The latex sample from each clone was obtained from the bulking of the regular tap-

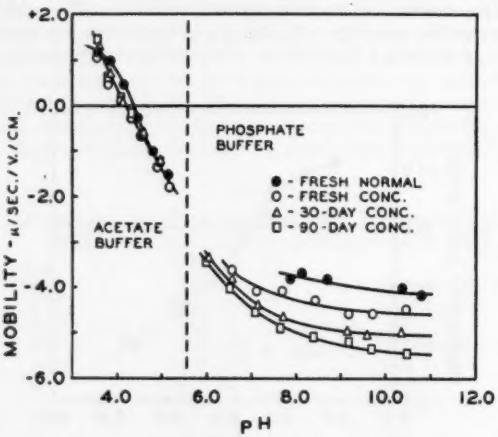

FIG. 5.—Effect of latex aging on mobility-pH relation.
Buffer ionic strength 0.02
War. 4 latex

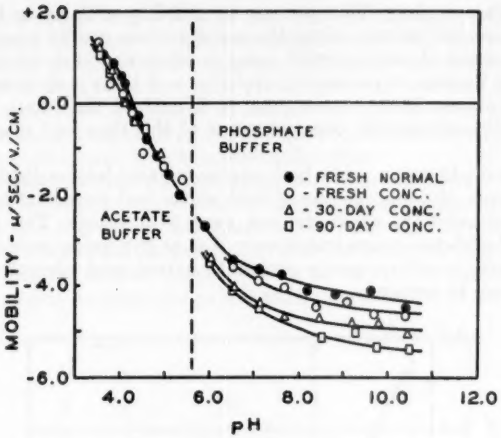

FIG. 6.—Effect of latex aging on mobility-pH relation.

Buffer ionic strength 0.02
P.B. 186 latex

ping of approximately 50 15-year-old trees tapped on a half-spiral, alternate daily basis. The feed latexes were diluted to 26 per cent total solids before centrifuging. In Figures 5 and 6 the mobilities of these concentrates are plotted as a function of pH, along with the values obtained on the fresh normal latex of a typical free trom each clone. The mechanical stability and potassium hydroxide number of the aged concentrates are presented in Table II.

Several points of interest are brought out by these data. First, despite the very much greater mechanical stability of the P.B. 186 concentrate, there is no significant difference in mobility between the two clones when the concentrates

TABLE II

PROPERTIES OF WAR. 4 AND P.B. 186 CONCENTRATES

Clone	Total solids	Mech. stability (sec.)		KOH no.		% NH_3
		30-day	90-day	30-day	90-day	
P.B. 186	62.1	1300	2800	0.45	0.53	0.70
War. 4	61.5	450	810	0.59	0.66	0.70

are compared at corresponding aging periods and pH values. However, the mobility of the P.B. 186 fresh normal latex is definitely higher than the War. 4 sample throughout the high pH range by about 0.3 pH unit. Clonal differences in mechanical stability, on the other hand, do not become apparent until after a certain amount of aging has occurred. For both clonal concentrates in the high pH region the mobility increases with the age of the latex, just as the mechanical stability does. This increase in mobility is probably the result of hydrolysis of esters of high molecular weight fat acids and of other fat materials, with the consequent formation of ammonium soaps. These charged soap anions will be adsorbed on the uncovered portion of the rubber particle surface, displace proteins already present on the surface, or react with the proteins to form

a soap-protein complex. This increase in mobility with aging becomes less marked at lower pH values, where the soaps are less readily adsorbed.

As the increase of mobility with aging is relatively much smaller than the corresponding increase in mechanical stability, and there is no clonal difference in mobility between these concentrates, it is evident that there is no useful correlation between mobility measurements of this type and mechanical stability.

In the lower pH region, while both unconcentrated latexes displayed normal isoelectric points, the concentrates of both clones had somewhat lower isoelectric points, about 4.15, which did not vary with aging. The mobility-pH relations of the 90-day concentrates show that at this aging period the rubber particle covering is still primarily protein in nature, and adsorption of soap is relatively minor in amount.

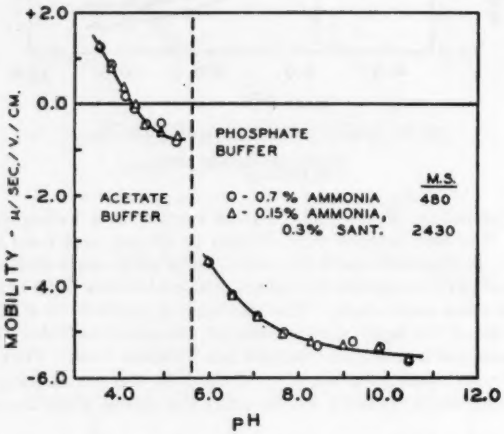

FIG. 7.—Effect of Santobrite on mobility-pH relation.

Buffer ionic strength 0.02
Av. 152 latex

Santobrite Latex.—Concentrated latexes preserved with 0.3 per cent Santobrite (sodium pentachlorophenate) and 0.15 per cent ammonia possess mechanical stabilities considerably higher than those preserved with 0.7 per cent ammonia alone (all concentrations based on total latex). An experiment was made to determine whether an increase of stability resulting from Santobrite preservation could be correlated with a higher electrophoretic mobility. The increase in stability from the presence of Santobrite varies widely among the different clones; consequently Av. 152, which exhibits the greatest increase, was chosen for this experiment.

The feed was obtained from approximately fifty 15-year-old trees tapped on the usual half-spiral, alternate daily system. A sample of concentrate prepared on a laboratory centrifuge from this feed was divided into two portions. One portion was ammoniated with 25 per cent ammonium hydroxide to 0.7 per cent ammonia; to the other portion 0.3 per cent Santobrite was added, along with sufficient 25 per cent ammonium hydroxide and water, so that the am-

monia concentration would be 0.15 per cent and the total solids of the two portions would be equal. These two samples were then stored for 30 days, after which the mobilities and mechanical stabilities were compared.

The results are shown in Figure 7. Despite the fact that the Santobrite-preserved sample had a mechanical stability of 2430 seconds against 480 seconds for the ammonia-preserved sample, the two latexes had an identical mobility-pH relationship well within experimental error.

This provides another instance of the lack of any good correlation between mechanical stability and electrophoretic mobility. If the mobility is considered to be a function of the electrical charge on the rubber particles and of the ionic atmosphere in which the particles exist, then the reason for this lack of correlation may be sought in other properties such as viscosity or particle size. However, the mobility as measured in this study is a function of the ionic strength

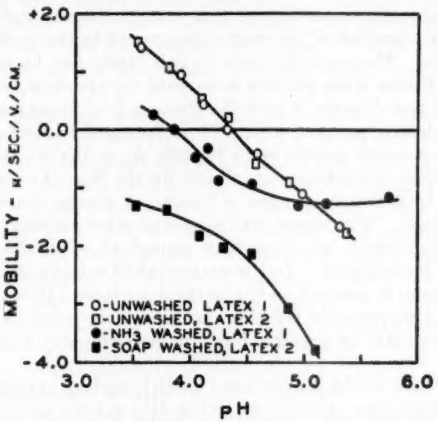

FIG. 8.—Effect of washing on mobility-pH relation.

Buffer ionic strength 0.02
Av. 50 latex

of the buffer solution in which the rubber particles are suspended, but not to such a great extent of the ionic atmosphere of the latex serum. The variation of mechanical stability among the clones may result primarily from a variation in the development of serum ionic strength from clone to clone. Likewise, the presence of Santobrite in the serum may inhibit the formation of ionic material in latexes preserved with this substance. Because of the uncertainty of determining the ionic strength of a latex serum, mobility measurements in the presence of serum were not made, but they might very well reveal significant differences which similar measurements in the presence of buffer solution of known ionic strength do not.

Washing of Latex Particle.—In order to determine to what extent the surface characteristics of the latex particle could be altered by washing, two samples of latex, obtained on different days, from 1000-gallon bulkings of predominantly Av. 50 latex, were centrifuged eight times with redilution of each cream before the following concentration step. In the first sample, these dilutions were made with 3 per cent ammonium hydroxide solution, and in the

second case with a soap solution which was 2 per cent in oleic acid and 3 percent in ammonia in excess of that required to neutralize the oleic acid. The mobility-pH relation was determined both before washing and on the eighth cream, in all cases at a buffer ionic strength of 0.02. The results are shown in Figure 8.

Both samples before washing had an isoelectric point of 4.35. The latex washed with ammonium hydroxide solution had a much lower value of 3.86, while the sample washed with soap was negatively charged at all pH values down to 3.5, the lower end of the pH range studied. The decrease in the pH value of the isoelectric point for the ammonia-washed sample shows that even such drastic washing as this is not sufficient to remove all the stabilizing material originally present on the particle surface.

The isoelectric point of this ammonia-washed sample corresponds very closely to that of the "Protein B" which Bondy and Freundlich[8] isolated from the serum of ammonia-preserved Hevea latex. If the surface of the washed particle is covered predominantly with this protein, then at high pH values it is the most strongly adsorbed of the materials present in the surface layer of the unwashed particle. The mobility data of this study can be explained by assuming that the Hevea latex particle is covered by amounts, which vary from clone to clone, of this Protein B and the Protein A of Bondy and Freundlich, which has an isoelectric point of 4.55. Thus the particle surface in the War. 4 latexes would be covered mostly with Protein A, in the Av. 152 latexes with Protein B. The low isoelectric point shown by the War. 4 concentrate of Figure 5 may result from the desorption of Protein A during concentration in the presence of ammonia. The presence of sterols or other material of very low isoelectric point is apparently not important enough to affect the electrophoretic characteristics of Hevea latex. In the soap-washed sample, it is evident that a large amount of soap is present on the particle surface. However, the tightly adsorbed material responsible for the low isoelectric point of the ammonia-washed sample may still be present, but now covering only a minor fraction of the surface.

The representation of the Hevea latex particle surface outlined here is probably an oversimplification of the case, but it does satisfy all the mobility data obtained in this work. The most fruitful source of information on this subject in the future will probably be chemical investigations of the proteins associated with both the rubber particle and with the serum. Serum components could affect the mechanical stability of latex by altering the electrical double layer distance, without exerting any profound influence on the charge of the particle. It is felt that a knowledge of the serum components and the changes they undergo during aging of latex concentrate is of the greatest importance in controlling such a variable substance as Hevea latex in its many technological applications.

ACKNOWLEDGMENT

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REFERENCES

[1] Abramson, Moyer, and Gorin, "Electrophoresis of Proteins", Reinhold Publishing Corporation, New York, 1942.
[2] Briggs, *Ind. Eng. Chem. Anal. Ed.* 12, 703 (1940).
[3] The conductivity bridge was Model RC-BC of Industrial Instruments, Inc.
[4] Komagata, Researches Electrotechn. Lab. Tokyo, No. 348 (1933).
[5] This apparatus was a Beckman Model G.
[6] Moyer, *Am. J. Botany* 21, 293 (1934).
[7] Kidder, *India Rubber World* 124, 563, 699 (1951).
[8] Bondy and Freundlich, *Compt. rend. trav. lab. Carlsberg* 22, 89 (1937).

THE FLOCCULATION OF DILUTE LATEX BY ZINC SULFATE *

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INTRODUCTION

The quality of ammonia-preserved latex is currently evaluated in the rubber industry by tests which serve to indicate, first, its mechanical stability to the inevitable shocks and friction to which it is subjected during transfer from one container to another and during mixing and, in addition, its chemical stability toward destabilizing agents, such as zinc oxide and salts of polyvalent metals in general.

In the case of field latex which has just been collected on a plantation, any information concerning its stability is always of great importance, yet up to the present time such information has remained essentially qualitative because of a lack of any precise methods of measurement. Furthermore, the stability of a latex is manifest in quite different ways in the different stages of its processing and in the methods employed for destabilization. Of particular significance are (1) the rapidity with which field latex coagulates spontaneously in the air as a result of the action of enzymes and bacteria present in the latex; (2) its more or less pronounced tendency to coagulate slowly throughout the entire mass or in successive fractions as a result of the action of coagulating agents such as acids and salts, and (3) its degree of sensitivity to heat and to mechanical agitation. This last factor in the destabilization of latex is of great importance in the concentration of latex by centrifugation.

These different aspects of stability are apparently independent of one another, and it should be mentioned at this point, to avoid further confusion, that the conclusions concerning chemical stability, which are the special concern of the present work, bear no relation whatsoever to mechanical stability or to spontaneous coagulation.

It was in connection with attempts, during the year 1951, to prepare special types of crude rubber that the Rubber Research Institute of Indochina became fully aware of the practical importance of a test of chemical stability which would be applicable to field latex at any time when it might be necessary to make some sort of change in the process being used for the preparation of crude rubber which might render difficult the proper control of coagulation.

In the course of experiments concerned with the development of such a test, it was found that, contrary to earlier observations made on relatively concentrated latexes[1], there is a remarkable discontinuity in the colloidal equilibrium when increasing proportions of a salt of a polyvalent metal, such as zinc, are added to sufficiently dilute latex within a certain favorable range of temperatures. The phenomenon is manifest both with fresh latex and with latex preserved with ammonia, but in somewhat different ways in the two cases, and not in the same range of dilution, nor in the same temperature range.

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With the hope that the critical amount of zinc salt added to latex at the point where this discontinuity appears would be an index of chemical stability, a study was undertaken of its change as a function of the temperature, of the dilution, and of the pH value for some field latexes of known plant origin and for two samples of latex preserved with ammonia. Under these conditions it was possible to establish arbitrarily definite testing conditions and, in each case, to compare the indexes obtained.

The reproducibility and discriminatory power of the method appeared to be satisfactory, but the number of samples examined up to the present time is insufficient to judge to what extent the method can be of definite aid to the latex technologist and can be used as a criterion of the chemical stability of latex. A more or less analogous method has, as a matter of fact, been recently used with success as a means of comparison of the stability of polyvinyl chloride latexes[2].

Any theoretical explanation of the phenomena observed during flocculation would necessitate a large number of additional experiments, which could not be carried out in the course of this relatively short preliminary study.

CHOICE OF DESTABILIZING AGENT FOR DILUTED LATEX

Before describing the characteristic reactions of latex to which zinc sulfate has been added, it is well to point out why this particular salt was chosen in preference to other salts of polyvalent metals which are known to have marked destabilizing effects on latex, such, for example, as calcium salts and aluminum salts[3]. The reason for the choice of zinc sulfate is that zinc plays an essential role in the technology of latex, since one of the principal methods of heat sensitization is based on the transformation, in the serum, of zinc oxide into soluble zinc salts[4]. It was to be hoped, therefore, that, by confining oneself to this same cation, it would be possible to establish a better correlation between the new stability index and certain other stability tests already applied to preserved latex which are based on measurement of the time of coagulation when hot after addition of a known quantity of zinc oxide[5] or of ammoniacal zinc acetate[6].

Because of lack of time, however, it has not been possible to study in detail the influence of the nature of the cation on the characteristics of the flocculation of diluted latex, but it is probable that metals other than zinc could be employed in the determination of the stability index.

The nature of the anion is much less important than that of the cation, at least provided that the salt is sufficiently soluble, since no appreciable differences in effects are observed when zinc sulfate is replaced by zinc acetate. However, solutions of the latter have the disadvantage of causing a deposit which dirties the burettes and this salt is, therefore, less satisfactory. Attempts were made without success to use formic acid and acetic acid, but in each case coagulation is a progressive phenomenon, whatever the experimental conditions, with no point of discontinuity in the colloidal state for a critical quantity of acid.

CHANGE OF APPEARANCE OF DILUTED LATEX RESULTING FROM THE ADDITION OF ZINC SULFATE

The technique employed in the experiments to be described involved the addition to latex, which had been diluted to increasing degrees with water, of increasing proportions of a solution of zinc sulfate. This solution was run from a precision burette into a beaker containing the latex maintained at a constant temperature. The zinc sulfate solution must be of a sufficiently high concen-

tration so that the latex is diluted to only a negligible degree during the test. Dispersion of the zinc sulfate uniformly throughout the latex is attained by agitation.

In addition to changing the dilution and the temperature of the latex, the initial pH value of the latter can be changed, before addition of the zinc sulfate, by adding the proper amount of sodium hydroxide or formic acid. The behavior of a latex, which can be watched with the aid of an electric lamp placed close to the beaker, depends, therefore, on the nature of the latex, on its dilution, on the temperature, and, to a lesser degree, on the initial pH value, provided that the latter is higher than a certain value which varies from 5.5 to 6, depending on the conditions.

Below this initial pH value, latex may coagulate without any zinc sulfate having been added.

FLOCCULATION OF COMMERCIAL CENTRIFUGED LATEXES PRESERVED WITH AMMONIA

When commercial centrifuged latex preserved with ammonia and of concentration normally close to 60 per cent is diluted to increasing degrees, flocculation caused by zinc sulfate can show two quite distinct effects.

(1) *At concentrations higher than 2 per cent.*—Either simple thickening or successive local points of coagulation, with no distinct discontinuity during the course of destabilization, which is progressive throughout the process.

(2) *At concentrations lower than 2 per cent.*—When the temperature is higher than 60° C, floccules appear, the formation of which progresses in proportion to the addition of zinc sulfate. In the temperature range from room temperature to 60° C, the latex becomes more turbid and starts to thicken as soon as the first drops of destabilizing solution are added; then, on continued addition of the latter, a stiff waxy transparent layer forms on the surface of the latex and the viscosity of the latter decreases. At this stage, the latex, although altered by the addition of the zinc sulfate, appears to be in a stable colloidal state, since it shows no further change when let stand by itself. On the contrary, above a certain critical quantity of zinc sulfate, this stability is abruptly destroyed, and there is observed, just below the transparent waxy layer, white spots, which rapidly descend into the liquid and cause the latter to lose its milky appearance. These spots then increase in size very rapidly and form floccules, which remain largely disseminated throughout the serum.

FLOCCULATION OF FIELD LATEX

The reactions of field latex when zinc sulfate is added differ from those of latex preserved with ammonia, both in their character and by the rapidity of the changes which take place at any given temperature.

(1) *At concentrations higher than approximately 5 per cent.*—Flocculation brought about by increasing amounts of zinc sulfate is progressive, irrespective of the initial pH value or of the temperature.

(2) *At concentrations below approximately 5 per cent.*—Only in a relatively high and limited range of temperature, *viz.*, 75–85° C, is there evident, in the course of flocculation, any discontinuity which is well defined enough to be used as a measure of the chemical stability. At temperatures above 85° C, successive local points of coagulation are observed, as in the case of preserved latex.

At temperatures below 75° C, changes in diluted field latex are slow, even when the amount of zinc sulfate added is relatively great.

In the intermediate range of temperatures, the temperature can be varied from 75° to 85° C without altering appreciably the progress of flocculation. However, the changes are not strictly the same, but depend on whether the initial pH value of the latex is higher or lower than a certain value, which varies from 6.1 to 6.5, depending on the origin of the latex. In the higher range of pH values, it has been found that latex thickens gradually from the first moment that the zinc sulfate solution is added, while the stirrer causes a creamy foam to form. This cream is then transformed into a light white coagulum, while the remainder of the latex reverts to a more fluid state. During this period, the latex does not change any further unless more zinc sulfate is added.

On the contrary, a spontaneous and rather rapid change takes place as soon as a certain critical amount of zinc sulfate has been exceeded. This is manifest by the sudden appearance, on the surface of the latex, of shining spots which give the surface a characteristic granitelike aspect. Without any further addition of zinc sulfate being necessary, there is then observed a progressive formation of floccules, which swim in the serum; the latter becomes progressively clearer, so that by running the stirrer gently to unite the floccules, a single coagulum is formed, usually in less than two minutes.

When the initial pH value of the latex is lower than 6.1–6.5, a further complication arises, as a result of precoagulation of a yellow fraction, which has already been encountered in the centrifugation of normal field latex[7]. From the beginning of the addition of zinc sulfate, this yellow fraction separates in the form of coagula of considerable size, depending on the plant origin of the latex and on the rate of addition of the zinc sulfate. The remainder of the latex remains white and fluid to the point of formation of the granitelike surface described above, which indicates spontaneous flocculation and which progresses in the same way as it does when the initial pH is alkaline.

Some field latexes which are particularly unstable, such as the latex of clone GL.1, form an exception to the mechanism of flocculation described above, in that they coagulate when simply heated, without the addition of zinc sulfate, and irrespective of the initial pH value.

MEASUREMENT OF THE SALT INDEX

An attempt was then made to study quantitatively the phenomenon of flocculation by systematic measurements of the *salt index*, that is, the weight of zinc sulfate just necessary to bring about a break in the colloidal equilibrium of 100 grams of diluted latex, the various aspects of which have just been described.

The amount of zinc sulfate which must be added has been found to be practically proportional to the weight of the latex sample, provided that this is not much greater than 100 grams, so the tests were carried out with samples of this size, which gave maximum precision of measurement.

The zinc sulfate employed was a pure grade, crystallized with 7 H_2O molecules. The destabilizing solution was prepared from this salt as a 3 per cent solution, which was placed in a 5-cc. precision burette. The temperature of testing was 40° C for all samples of ammonia-preserved latex and 80° C for all samples of field latex.

By repeating several times the flocculation test of the same diluted latex and under rigorously controlled and identical conditions, it was established that the amounts of zinc sulfate to reach the critical point of flocculation did not, in

general, deviate more than 3 per cent, provided that the tests were carried out within the favorable range of concentration. This quite satisfactory precision is explainable by the sensitivity of the latex in the neighborhood of the critical point, where the addition of one or two drops of solution changes radically the appearance of the latex.

INFLUENCE OF VARIOUS FACTORS ON THE SALT INDEXES OF FIELD LATEXES AND AMMONIA-PRESERVED LATEXES

AGE OF THE LATEX

One of the important factors which had to be taken into account in studying the susceptibility of the salt index to different influences was, naturally, the age of the latex. It might, in fact, be expected that, at least in the case of field latex, the changes which lead finally to spontaneous coagulation would manifest themselves by a change of the salt index with time. But it was found that this is in no way true, and that it is possible to test a given sample of undiluted field latex at any convenient time during a period of several hours without fear of any change of its behavior on the addition of zinc sulfate. However, in the case of ammonia-preserved latex, care must be taken to avoid evaporation of this alkaline agent. In general, any effect of the age of a latex is attributable only to slow changes which the latex undergoes during storage.

On the other hand, the time of aging becomes of importance when a latex has been diluted to a concentration below 20 per cent. In this case, with conditions otherwise the same, the salt index remains, in fact, constant for only about one hour after dilution of the latex, and then decreases progressively. For this reason, samples of latex should not be diluted to a low concentration for the purpose of measuring the salt index until just before the time of testing.

CONCENTRATION OF THE LATEX

Despite the buffer effect of a latex, dilution changes to only a very small extent the pH value of the latex. Since, moreover, the salt index is very sensitive to the initial pH value, it is obvious that the influence of the concentration can be correctly studied only if the pH value is the same throughout a given series of tests. This condition is attained by addition to the diluted latex, just

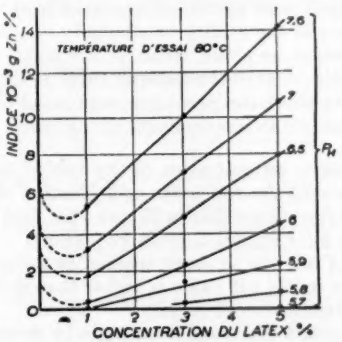

FIG. 1.—Influence of the dilution of a field latex on its salt index at constant pH value. Initial concentration 33.5 per cent.

before the measurement is made, of the necessary amount of alkali (sodium hydroxide or ammonia) or of acid (formic acid or acetic acid). The salt index, found experimentally, as a function of the concentration of dry rubber is shown in Figure 1 for a field latex from clone W_4, while Figure 2 shows the same relation for a latex centrifuged after seven days and preserved with ammonia in the usual way.

The curves of each of these two latexes are not strictly comparable because they do not represent as a whole the same ranges of concentration of dry rubber. They do show, however, that the salt index is, in general, an increasing function of the concentration, except for ammoniated latexes whose initial pH values are less than 8 or 9. In the region of very high dilutions, the curves are represented

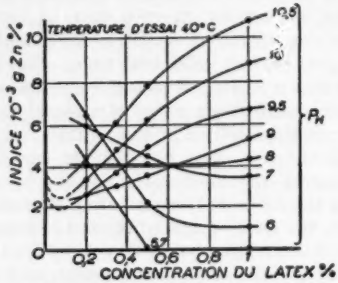

FIG. 2.—Influence of the dilution of an ammoniated latex (centrifuged seven days earlier) on its salt index at constant pH value.

in broken form as if they passed through minimum points. As a matter of fact, below 1 per cent concentration for field latex and 0.1 per cent concentration for ammoniated latex, the salt index depends to an increasing degree on the rapidity of measuring; in fact, to such a degree that its measurement finally loses any significance.

INITIAL ALKALINITY OR ACIDITY OF LATEX

The addition of a solution of zinc sulfate to latex always brings about a certain decrease of the pH value, as exemplified by the two cases shown in Figure 3, which represent a field latex and an ammoniated latex. As a means of characterizing the influence of the acidity or alkalinity of a latex on its salt index, an arbitrary choice might be made, either of the initial pH value just before addition of the zinc sulfate, or of the final pH value at the point of flocculation. The results obtained by this latter procedure were found to be somewhat erratic, so recourse was had simply to measurement of the initial pH value of the latex at room temperature.

Maintaining the same concentration of dry rubber in a given series of experiments, curves showing the salt index as a function of the initial pH value are obtained, of the type exemplified in Figure 4 for field latex and of the type exemplified in Figure 5 for ammonia-preserved latex.

The curves of field latex in all cases descend as the acidity of the latex increases, and when the initial pH value is higher than 6–6.5, the change of the salt index begins to decrease more rapidly.

The curves of ammonia-preserved latex begin by decreasing from a point of very high alkalinity to the point of neutrality, then pass through minima, and finally pass through maxima in the acid range.

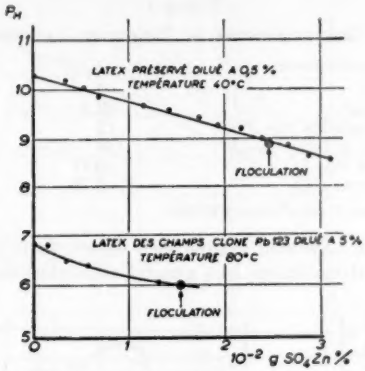

FIG. 3.—Examples of the pH value as a function of the amount of zinc sulfate added to 100 grams of latex.

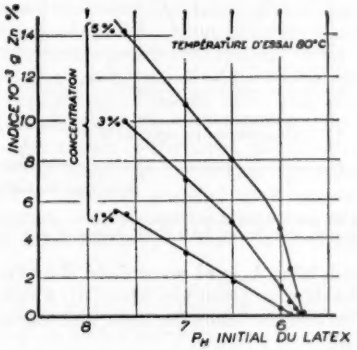

FIG. 4.—Influence of the initial pH value of field latex on the salt index of the latex at constant concentration. Initial concentration 33.5 per cent.

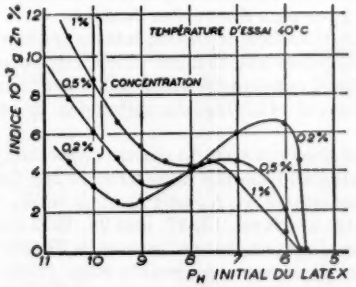

FIG. 5.—Influence of the initial pH value of preserved latex, seven days after centrifuging and at constant concentration, on the salt index of the latex.

TABLE 1

IMPORTANT CHARACTERISTICS OF PRESERVED LATEXES A AND B

Ammoniated latex	A	B
Age in days	7	105
Concentration	62.5	60.9
Chemical stability (sec.)*	12	36
Mechanical stability (sec.)*	146	1157
KOH index (%)	0.77	0.58
Free ammonia (%)	0.78	0.95

* According to the French Rubber Institute Method.

Because only two preserved latexes were tested, there is, of course, no certainty that this final maximum is a general characteristic of latex preserved with ammonia.

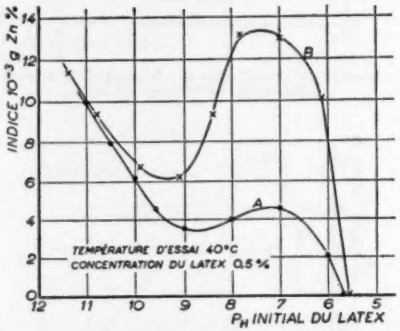

FIG. 6.—Curves of the salt indexes of two preserved latexes of different ages. Latex A 7 days after centrifuging; latex B 105 days after centrifuging.

The anomaly which latex A, aged seven days, shows to only a slight extent, is very pronounced for another preserved latex (B), which had been centrifuged and ammoniated three months before the tests, and was much more stable than latex A (see Figure 6).

AGRONOMIC FACTORS

Figure 7 assembles a set of curves showing the salt index as a function of the initial pH value for seven samples of field latex collected in March 1952 and in each case diluted to 5 per cent dry-rubber content.

These tests do not, therefore, represent latexes of very different origins and give no opportunity to follow any changes which might occur over long periods. Therefore the provisional conclusions which follow are to be regarded as indicative of the importance of studying the salt index in relation to agronomic factors.

(1) The salt index does not seem to change appreciably from day to day in the case of latexes gathered from the same trees during the dry season. Thus, the curves of the three latexes A_1, A_2, and A_3 of clone W_4, which were collected on the respective dates of March 13, 17, and 24, 1952 from the same trees of field V, form a confused system, as can be seen in Figure 7.

(2) The salt index decreases considerably when there has been rain before collection of the latex; e.g., Table 2 shows that, for the second sample cited, the salt index was 20 per cent lower following a rain the night before.

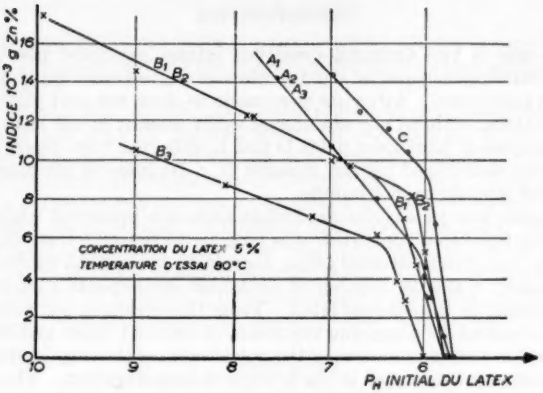

FIG. 7.—Curves of the salt indexes of various field latexes.

With each of the fourteen latexes listed in Table 2, the concentration was reduced to 5 per cent and the initial pH value to approximately 6.7 by diluting the latexes with 0.004 per cent aqueous formic acid.

(3) As is evident in Table 2 and Figure 7sa, the lt indexes of latexes of different plant origins cover a wide range of values. The discriminatory power of the method is, therefore, quite satisfactory.

(4) The period of exploitation of the trees, though known to be a factor which favors the stability of latex, has in addition a considerable effect on the salt index. The indexes of latexes B_1 and B_2 from trees, tapping of which was started in 1942 (field V) are, in fact, much higher than those of latex B_1 obtained from trees of the same clone Tj.1, but from younger trees which were not tapped until 1950 (see Figure 7).

The identity of the clone is perhaps evident in the parallelism of the curves representing the salt index as a function of the pH value of latexes B_1 and B_2 on the one hand and of latex B_3 on the other.

TABLE 2

EXAMPLES SHOWING THE SALT INDEXES OF DIFFERENT FIELD LATEXES
(Concentration 5 per cent, initial pH value 6.7, temperature 80° C)

Latex	Date in 1952 collected	Weather	Concentration of rubber (%)	Salt index (10^{-3} g.-% zinc)
W.4	Mar. 13–24	dry	33.5–39.3	9
W.4	Mar. 31	night rain	—	7.2
Tj.1 (field V)	Mar. 25 and 27	dry	46.3–48.5	9.5
Tj.1 (field 3–5)	Mar. 25	dry	41	6.2
Avros 255	Mar. 28	dry	32.6	12.8
Avros 188	April 4	dry	33.8	15.8
Avros 188	April 5	dry	35	15.3
Avros 163 ill.	April 7	dry	41.2	13.8
Avros 163 ill.	April 8	dry	37.5	10.9
Average (field V-B)	April 8	dry	44.5	10.7
Field V-B	April 11	dry	46.7	11.3
GL.1	March 24	dry	49.3	0
Bulk ¼	April 4	dry	43.8	9.45
Field V-A	April 10	dry	47.8	11

CENTRIFUGATION

In the case of two ammonia-preserved latexes examined previously, the effects of centrifugation and of storage when preserved with ammonia are evident at the same time. Attempts were made to show the part played by centrifugation alone, without any stabilizing agent present in the latex. To this end, two samples of latex from fields D and E, collected from clones Avros 186 and W_4, were centrifuged for ten minutes in a Huguenard ultracentrifuge at about 70,000 revolutions per minute.

In the same way as was observed when ammonia-preserved latex[8] was centrifuged with this same apparatus, it is possible to separate from the serum of field latex a ring of concentrated cream containing fewer small rubber particles, and particularly a smaller number of nonrubber components, such as proteins, than are present in the original latex. From this cream, a purified latex can readily be prepared by dispersing the cream in distilled water and filtering the dilute latex thus obtained to remove the outside skin of the ring described above, which has already coagulated in the process of centrifugation. The salt index

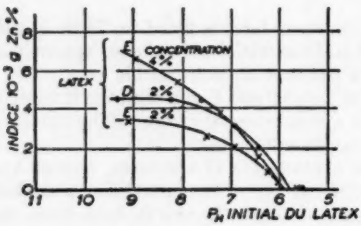

FIG. 8.—Curves of the salt indexes of centrifuged field latexes.

Latex	Clone	Field	Initial concentration	Temperature
D	Avros 186	3/5	45.6	70° C
E	W_4	3/1	39.3	70° C

of this purified latex can then be determined, but the most favorable temperature is, in this case, a little lower than that for normal latex, i.e., 70° C instead of 80° C.

Figure 8 shows these salt indexes as a function of the initial pH values at constant concentration. A comparison of these results with those shown in Figure 1, which likewise are for latex from clone W_4, indicates that purification by ultracentrifugation is accompanied by great decreases, almost 50 per cent in fact, of the salt indexes for the same concentrations and pH values.

However, there is not a complete levelling of the properties, since, even after ultracentrifugation, the salt indexes of latex D are considerably higher than those of latex E from another clone.

Finally, partial removal of the nonrubber components by ultracentrifugation seems to lead to a notable simplification of the curves representing the salt index as a function of the pH value. It is no longer possible to distinguish two well defined regions, according to whether the initial pH value is in the acid range or in the alkaline range, as in the case of field latexes or the two ammonia-preserved latexes. Instead, the salt index decreases in proportion to the decrease of the pH value in accordance with a curve which follows a regular course throughout the range of pH values examined.

BUFFER EFFECT

The decrease of the salt index of a field latex by ultracentrifugation must be explained, at least in part, by the reduced buffer effect which characterizes such purified latexes.

With diluted field latexes, the addition of a buffering agent has, in fact, a considerable influence on the mechanism of flocculation by zinc sulfate, although this influence does not appear to be wholly dependent, for a given pH value, on the chemical composition of the buffering agent. Thus it was found impossible to coagulate a field latex of normal character, which had been diluted to 5 per cent concentration, by addition of a buffer solution of pH 7. When the same latex, again diluted to 5 per cent concentration, was treated with a buffering solution of pH 5 and thus brought to pH 5.7, flocculation at 80° C was effected only by addition of 0.0256 gram-per cent of zinc, in contrast to the spontaneous coagulation of a latex simply diluted with an aqueous acid.

DISCUSSION

In view of a lack of any definite facts on relations which may exist in practice between the salt index and chemical stability in the broad sense, we shall restrict ourselves to a few hypotheses, which, if they can be confirmed by additional experiments, will make possible an understanding of the essential nature of the flocculation of diluted latex by a soluble zinc salt, as described in the present paper.

Other investigations of the gelation by zinc oxide of ammonia-preserved latex have shown that the colloid is destabilized as a result of the formation, under certain conditions, of soluble zinc salts, formed from the zinc oxide present[3]. The zinc ions present in the serum react with the organic ions adsorbed on the surface of the latex globules, with formation of insoluble soaps[4]. Since the number of ionized particles fixed on the globules is thereby diminished, it is conceivable that the electric charge on these globules and, consequently, the stability of the colloid must likewise be diminished.

The preceding chemical theory is, however, contested by certain authors, who explain the destabilization of latex by a more classic mechanism of an essentially physical nature, i.e., the electrosorption of the zinc ions on the particles of rubber and the resulting change of electrokinetic potential.

Whatever is the correct view, one is confronted with two hypotheses respecting the essential significance of the total amount of zinc necessary to reach the threshhold beyond which the effect of a small increase of the concentration of zinc in the latex becomes the determinant factor.

If the substances adsorbed on the surface of the rubber particles are conceded to play a major part in these phenomena, it may then be assumed that at least most, if not all, of the zinc is adsorbed in proportion to the amount added. If this is so, then the major part of the zinc must be expected to remain in the coagulum when the latter is separated from the serum at the end of an experiment. Now, determination of the zinc remaining in the serum of a field latex, diluted to 5 per cent rubber content, after coagulation of 100 cc. of the latex by the critical amount of zinc sulfate, showed that 0.0068 gram of zinc was present in the serum when the total amount of zinc added was 0.0081 gram.

This result obviously suggests that substances in solution in the serum influence the salt index perhaps even more than do the adsorbed substances. According to this second hypothesis, the zinc could be adsorbed on the rubber particles only when the serum components which are susceptible of forming,

with zinc sulfate, compounds little or not at all dissociated have been completely neutralized. The salt index would then be a function on the one hand of the total concentration of these substances in the serum, and, on the other hand, of the physico-chemical equilibria which govern destabilization. In particular, dilution of the serum ought to result in a decrease of the salt index, and this has been found to be true in general experimentally in spite of the increase of the electric charge of the particles caused by dilution of the latex[10].

The effect of acids may be explained in the same way by preliminary neutralization of certain substances in the serum, independent of the reduction of the electric charge of the rubber particles. It can be regarded as extremely probable that several substances normally present in the latex are capable of insolubilizing zinc, and thus preventing the latter from exerting completely its destabilizing action.

The ammonia in preserved latex certainly reacts with zinc sulfate, with resulting precipitation of zinc hydroxide. At the low concentrations employed in the experiments described, the formation of zinc-ammonium complexes is, on the contrary, rather improbable, at least in any considerable amount[11]. In the case of field latex, the proportion of organic phosphates and natural soaps present in the serum seems likewise high enough for their reaction with zinc sulfate to absorb a notable fraction of the zinc[12].

Finally, the anomalies observed on the curves of the salt index as a function of the initial pH value may be explained by the complexity of the protective layer adsorbed by the rubber particles. From the work of Kemp and Twiss[10] on ammonia-preserved latex, the proportion of the total surface of the rubber particles occupied, respectively, by the resins and by the proteins should be functions of the pH value and of the degree of dilution of the latex. On the other hand, the small dissociation coefficients of fat acids of pH values lower than 8 or 9 go far toward proving that, in an acid latex, these adsorbed slightly ionized acids contribute hardly at all toward stabilization, and that stabilization is, instead, brought about chiefly by the proteins. In this case, it is possible to explain the two branches of the curves of the salt index as a function of the pH value; one where the protein influence predominates, i.e., in the acid range of the curves, and the other of a mixed character, where the lipoids and proteins participitate simultaneously in the stabilization. Ultracentrifuged field latexes, whose curves show only a single branch, would be an exception to this rule if it is assumed that they are stabilized throughout the range of pH values by only one protective mechanism.

CONCLUSIONS

The physico-chemical reactions which take place during the flocculation of latex by zinc sulfate are probably so complex that any hope of utilizing the salt index as a method of investigation of strictly scientific nature seems almost impossible. However, because of its rapidity and its simplicity, and also because of the shortcomings of all tests which have been used up to the present time, any test based on measurement of the salt index should be of great practical interest to rubber technologists. The essential condition for the successful development of such a test is, from this point of view, that dilution of the latex by the addition of a considerable proportion of water, which is indispensable for the identification of a well defined discontinuity during the progress of flocculation, does not bring about any considerable change of the colloidal properties of the latex.

If it is, *a priori*, certain that the adsorption equilibria between the surface of the rubber particles and the serum are functions primarily of the concentration, there is nothing to warrant the belief, *a priori*, that the nature and composition of the protective interfacial layers are, after dilution, the same as the corresponding relations in the case of normal latex or concentrated latex. It is to be hoped that the efforts now being made by the Rubber Research Institute in Indochina to correlate variations of the salt index of field latex with variations of the technological properties of centrifuged latex, measured by all the classic methods, will lead to success and will thereby furnish the latex technologist with a new tool.

SUMMARY

Within a particular range of temperatures and a particular concentration of rubber, the flocculation of diluted latex by a water-soluble zinc salt is characterized by a critical amount of zinc, termed the salt index, which is necessary and sufficient to destroy abruptly the colloidal equilibrium of the dispersion.

In the course of an investigation of a preliminary nature, measurements were made of the changes of the salt index as a function of the concentration and of the initial pH value of different field latexes and of two samples of latex preserved with ammonia.

The influence of centrifugation and of buffering agents was likewise investigated. On a theoretical basis, the phenomenon appears to be governed to a major degree by chemical reactions of the zinc with certain substances which are either in solution in the serum or are adsorbed on the rubber particles. From the practical point of view, a systematic investigation is underway to determine whether the salt index as thus defined can be accepted as a new test of the stability of fresh latex and preserved latex.

REFERENCES

[1] Belmas, *Rev. gén. caoutchouc* **26**, 505 (1949).
[2] Drinkwater and Payne, *Chem. & Ind.* **1951**, p. 683.
[3] De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur* **13**, 205 (1929).
[4] Kraay and van den Tempel, *Trans. Inst. Rubber Ind.* **28**, 144 (1952).
[5] Lepetit, *Rev. gén. caoutchouc* **24**, 390 (1947); *Trans. Inst. Rubber Ind.* **23**, 104 (1947).
[6] Tentative specification of the French Rubber Institute.
[7] Homans and van Gils, *Proc. 2nd Rubber Conf. London* **1948**, p. 292.
[8] Huret, *Rev. gén. caoutchouc* **25**, 124 (1948); Belmas, *Rev. gén. caoutchouc* **26**, 505 (1949).
[9] Lepetit, *Rev. gén. caoutchouc* **24**, 390 (1947); *Trans. Inst. Rubber Ind.* **23**, 104 (1947); Cassagne, *Rev. gén. caoutchouc* **28**, 39 (1951).
[10] Kemp and Twiss, *Trans. Faraday Soc.* **23**, 890 (1936); RUBBER CHEM. & TECHNOL. **9**, 551 (1936).
[11] Cassagne, *Rev. gén. caoutchouc* **28**, 39 (1951).
[12] Altman, *Rec. trav. chim. Pays-Bas* **65**, 919 (1946).

CONTRIBUTION TO THE DETERMINATION OF THE ABRASION RESISTANCE OF SOFT VULCANIZED RUBBER *

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INTRODUCTION

To predict the future performance of a vulcanized rubber compound actually amounts to making a forecast of its stress-strain properties, its color, its surface character, its elasticity, its recovery after stress, and its resistance to abrasion.

Today, a rating of the first five of these properties can be arrived at fairly satisfactorily by the aid of a large number of laboratory tests. Heat and oxygen aging, measurements of permanent deformation and of elastic fatigue, a study of ozone resistance, and observations of flex-cracking need merely be mentioned. Provided that the conditions of practical application are known, a more or less reliable estimate of the behavior to be expected in service can be made. This proviso, on the other hand, accounts for the fact that attempts are everywhere being made to improve existing methods of determining abrasion resistance.

Buist[1] has published an interesting survey of twenty-one abrasion testing machines. His conclusions on the unsatisfactory nature of the results of these various tests were abundantly confirmed at the ISO-TC-45 Conference at Akron in 1950. In view of the widespread use of the du Pont machine, it was then agreed to base international standards on this machine for the time being, although admittedly the results obtained do not agree at all well with practical experience[2]. Juve, Fielding and Grave[3] have also studied some of the other testing devices commonly used in American laboratories. The majority of these machines are rated as "passable", and many of them as "poor".

SOME FACTORS AFFECTING THE DETERMINATION OF WEAR IN RUBBER

1. Apart from the nature of the two parts in friction *viz.*, the rubber and the emery surfaces, the factor of resilience and hence the correct choice of load are of great importance. Under a light load, a springy compound will "jump", and thus escape a certain amount of wear. With the Dätwyler-Schiltknecht machine, for example, we have found that, when the load is doubled from 127 to 254 g. per sq. cm., the rate of abrasion is approximately tripled (Figure 1).

Abrasion of a soft rubber compound is more affected by change of load than is that of a harder vulcanized rubber.

The pressure acting on the specimen in various testing machines differs very widely[4], as shown in Table 1.

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In service, however, the load on rubber, for example for a tire or a shoe sole, is generally much higher. The more-or-less regular motion of the wheel or of the foot, and the rate of increase and decrease of load, play an important part. Since the abrasiveness of the emery parts used in testing machines is as a rule, considerably greater than that of a road surface, the testing machines generally operate at lower pressures.

2. There are also differences in the manner of application of the load, for example, parallel or perpendicular to the plane of the emery surface. Usually a

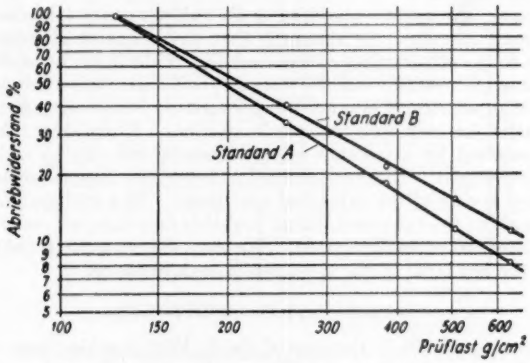

FIG. 1.—Abrasion resistance as a function of the test-load.

Ordinate—Abrasion resistance in percentage.
Abscissa—Test-load in g. per sq. cm.

constant weight is used, but there may be a spring or linkage which produces a variable load. The difference between these conditions emerges when the specimen, owing to irregular emery surface etc., is forced out of its normal position. Under constant weight, the force acting on the specimen remains the same. In the case of a spring (constant torque), the force increases in proportion as the specimen is pressed against the spring, so that the specimen promptly returns to its normal position. In the linkage of the Dätwyler-Schiltknecht

TABLE 1

LOAD APPLIED TO SPECIMEN IN VARIOUS ABRASION-TESTING MACHINES

Testing machine	Load (g. per sq. cm.)
U. S. National Bureau of Standards	353
Du Pont	450
Dätwyler-Schiltknecht	127

machine, on the other hand, the force decreases, thus allowing the elastic properties of the rubber to come into play to a larger extent.

Alternatively, specimens may be mounted in a fixed position in the plane of the emery surface. They then have little opportunity to "jump over" coarse emery particles, and are therefore worn more rapidly.

The importance of manner of load application is demonstrated by recently published data[4], according to which a du Pont machine converted from constant weight to constant torque showed considerably improved agreement with road tests in the rating of auto tires.

3. Motion of the specimen relative to the abrasive surface is another important factor. In some machines, as for example the Dunlop-Lambourn machine[6], the disc specimen and the emery surface are driven positively at different speeds. The resulting slippage naturally has the same scraping effect as the process of abrasion in other machines where only the specimen or only the emery surface is in motion. The only difference is that new elements of surface are continually being exposed to abrasion. This enables each particle on the surface of the rubber to be relieved by resilience to some extent before the emery surface can act again.

4. Of course, the *surface condition of the rubber specimen* is also of importance. It may, therefore, be assumed, that deviations of abrasion values is attributable to the efflorescence of wax and oil. Thus it has been thought that more reproducible results would be obtained with specimens subjected to extraction with an azeotropic ethanol-toluene mixture before testing[7]. However, this expectation has not been realized in all cases. Then again, the considerable labor required for extraction would be warranted only by a definite and reliable improvement. Extraction also involves difficulties in connection with the necessary drying of the extracted specimens. The oxidizing effect of the surrounding air on the extracted rubber probably causes even greater deviations than those intended to be eliminated. We have therefore preferred mechanical removal of the top layer of the specimen in each instance.

SPECIFICATION OF RESULTS

Until recently, results in the case of the du Pont machine were specified as volume loss per horsepower-hour. Today, however, the test results are ex-

TABLE 2

STANDARD COMPOUNDS FOR RUBBER ABRASION TESTS, AS RECOMMENDED BY ISO–TC–45

Composition (parts by wt.)	Standard A (tire-tread type)	Standard B (shoe-sole type)
Smoked sheet rubber	100	100
Zinc oxide	5	4
Stearic acid	3	3
Di-2-ethylhexyl phthalate	—	3
EPC black	50	60
Whiting	—	60
Benzothiazyl disulfide	1	—
Mercaptobenzothiazole	—	1
Sulfur	3	3
Phenyl-β-naphthylamine	1	1
Press-vulcanizing	40 minutes at 144° C	40 minutes at 153° C

$$\text{Abrasion Resistance} = \frac{S}{T} \cdot 100\%$$

S = volume loss of standard compound (cc.)
T = volume loss of specimen (cc.)

pressed in terms of abrasion resistance referred to a standard compound A or B[8], the abrasion resistance of the standard compound being taken as 100 per cent.

THE CARBON BLACK OPTIMUM

It has long been known empirically by rubber technologists that, in a rubber-carbon black mixture such as is used for tire treads, the best abrasion resistance

is obtained with a range of about 100:50 to 100:30 by weight of carbon black. Unfortunately, however, the various testing machines give highly contradictory results, with the exception of the Dunlop-Lambourn machine, which agrees closely with practical experience, and, accordingly, shows an optimum at about 50 parts of carbon black by weight[9].

Even the testing machine of the EMPA. (Federal Materials Testing Institute), St. Gallen, which—according to our information—acts on the speci-

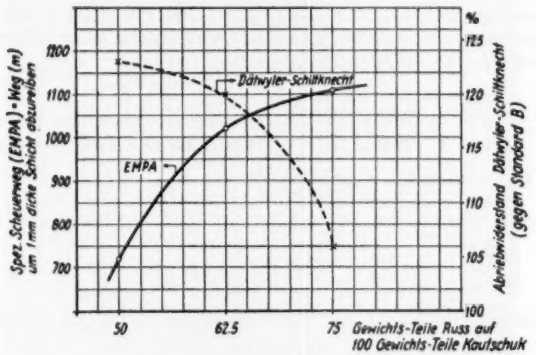

FIG. 2.—Comparison of abrasion resistance data obtained with two different testing machines.

Ordinate—Specific abrasion distance (EMPA) or distance (m.) to remove layer 1 mm. thick.
Abscissa—Parts of carbon black per 100 parts of rubber.
Ordinate—Abrasion resistance (Dätwyler-Schiltknecht) referred to Standard B.

men between two millstone-like plates, with sand as abrasive, incorrectly shows increasing abrasion resistance for carbon-black contents of 50, 62.5 and 75 parts per 100 parts of rubber by weight, while the corresponding results in the Dätwyler-Schiltknecht machine decrease (Figure 2).

THE DÄTWYLER–SCHILTKNECHT MACHINE

Since practical abrasion tests are generally very time-consuming and expensive, and also require thorough statistical planning and evaluation because of the large number of variables involved[10], we undertook to modify our

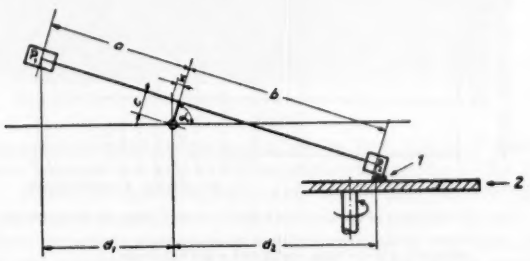

FIG. 3.—Schematic principle of the Dätwyler-Schiltknecht machine.
1. Rubber test-specimen. 2. Emery disc.

Schiltknecht-type abrasion-testing machine. The original Schiltknecht machine consisted of a device like a record-player, in which the rubber specimen was attached to the under side of the "pick-up" arm. This arm, while the emery paper "record" is turning, moves radially inward towards the center and back again to the periphery. The rotational speed is regulated by a differential gear in such a way that the specimen is abraded by the emery surface at a constant velocity (44 cm. per sec. or approximately 1.6 km. per hr.), regardless of its radial position relative to the axis of rotation.

The following simplified analysis demonstrates the effect of the lever arm. By way of rough approximation, we assume a weightless lever with two weights P_1 and P_2 at the ends (Figure 3).

$$x = c/\tan\alpha$$
$$d_1 = (a - x)\sin\alpha = (a - c/\tan\alpha)\sin\alpha = a\sin\alpha - c\cos\alpha$$
$$d_2 = (b + x)\sin\alpha = (b + c/\tan\alpha)\sin\alpha = b\sin\alpha + c\cos\alpha$$

Hence, for the torque:

$$P_2d_2 - P_1d_1 = P_2(b\sin\alpha + c\cos\alpha) - P_1(a\sin\alpha - c\cos\alpha)$$

$$\boxed{\text{Torque} = (P_2b - P_1a)\sin\alpha + (P_2c + P_1c)\cos\alpha}$$

If α becomes greater than 90°, both expressions on the right of the equation decrease.

$$\sin(90° + \beta) = \cos\beta$$
$$\cos(90° + \beta) = -\sin\beta \quad \text{for} \quad \alpha = 90° + \beta$$

Thus it is readily seen that the height of the specimen also has an effect on the load and, hence, on the rate of abrasion. But in the old Schiltknecht machine, as well as in the new Dätwyler-Schiltknecht type, there is another effect

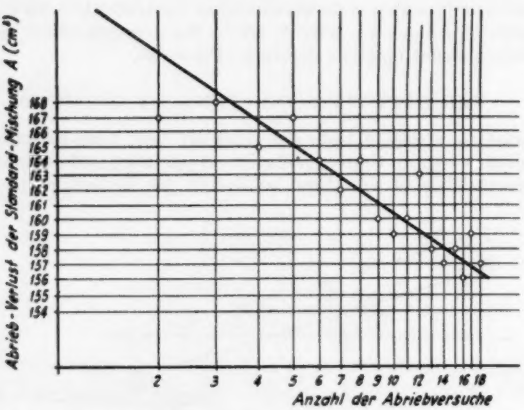

FIG. 4.—Decrease of the abrasive action of emery paper by repeated use.

Based on the equation of Buist: $y = ax^n$, where y is the abrasion, x is the time, and a and n are constants.

Ordinate—Abrasion loss of the Standard Compound A in cc.
Abscissa—Number of abrasion tests.

which depends on the height of the specimen. The specimen is held in a chuck, which compresses it. If only a small part of the specimen is outside the chuck, its surface is under stress, and therefore acts harder. On the other hand, the hardness of a large portion projecting from the chuck is less affected. It is, therefore, desirable always to adjust the specimens to the same height, with the aid of a gauge. Specimens that are too shallow should be cemented together.

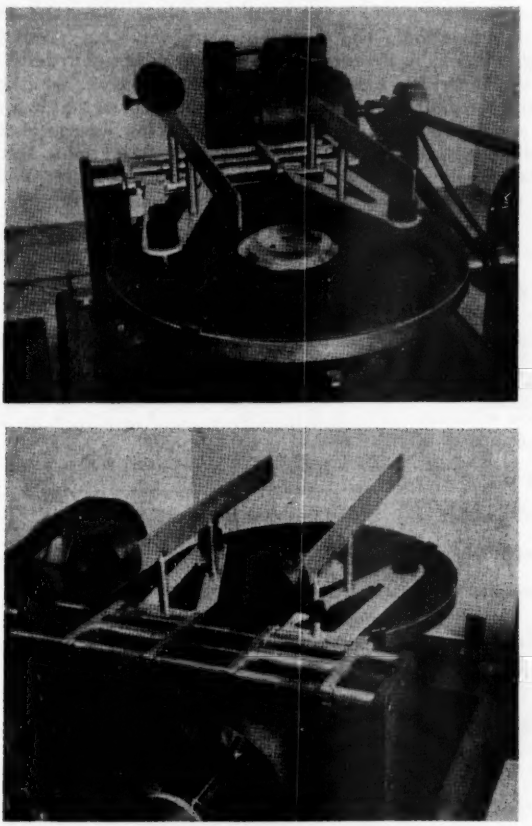

FIG. 5.—The Dätwyler-Schiltknecht abrasion testing machine.

The specimen is weighed before and after the test, which is generally performed at room temperature and at different loads according to the position of the weights. From the specific weight and weight loss, the volume loss in cubic centimeters is computed.

Our original technique consisted of first running two standard specimens, and then the test specimes, for 15 minutes each. The results were then referred to the average abrasion-resistance of the standard specimens. This

method helped compensate the difference between different emery-paper discs, but did not take care of any irregularities within individual discs. Study of such irregularities showed that the abrasiveness of the disc, with certain variations, decreases according to Buist's formula[11] (Figure 4).

Another slight improvement was, therefore, made by running one standard specimen at the beginning and the other at the end of a series of twenty. By plotting these two results on semilogarithmic graph paper with volume loss as a function of test sequence, it was possible to obtain the standard value S by graphical interpolation. Unfortunately, however, this promising method proved highly unreliable because of excessive irregularities within a given emery disc. To overcome all of these difficulties, we equipped our Schiltknecht testing machine with an additional independent pick-up arm, so that it is now possible to run the standard specimen simultaneously with the test-specimen (Figure 5).

This eliminates practically all deviates due to variable test conditions. Most of the remaining deviations are very likely due to unavoidable irregularities in the control specimen and test specimen themselves[12].

SOME TEST RESULTS OBTAINED WITH THE DÄTWYLER–SCHILTKNECHT MACHINE

Tire-tread compounds

TABLE 3

TIRE–TREAD COMPOUNDS, CORRESPONDING TO STANDARD COMPOUND A WITH VARIOUS CARBON–BLACK CONTENTS

Composition (parts by wt.)	Compound no. 1	2	3	4	5
Smoked sheet rubber	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	3	3	3	3	3
EPC black	15	30	45	60	75
Benzothiazyl disulfide	1	1	1	1	1
Sulfur	3	3	3	3	3
Phenyl-β-naphthylamine	1	1	1	1	1
Press vulcanizing	40 minutes at 144° C				

Under the test conditions we selected, we obtained a definite optimum at about 30 parts of carbon black by weight (Figure 6).

Shoe-sole compounds

TABLE 4

SHOE–SOLE COMPOUNDS, CORRESPONDING TO STANDARD COMPOUND B WITH VARIOUS CARBON–BLACK CONTENTS

Composition (parts by wt.)	Compound no. 6	7	8	9	10	11
Smoked sheet rubber	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4
Stearic Acid	3	3	3	3	3	3
Di-2-ethylhexyl phthalate	3	3	3	3	3	3
EPC black	—	15	30	45	60	75
Whiting	60	60	60	60	60	60
Mercaptobenzothiazole	1	1	1	1	1	1
Sulfur	3	3	3	3	3	3
Phenyl-β-naphthylamine	1	1	1	1	1	1
Press vulcanizing	40 minutes at 153° C					

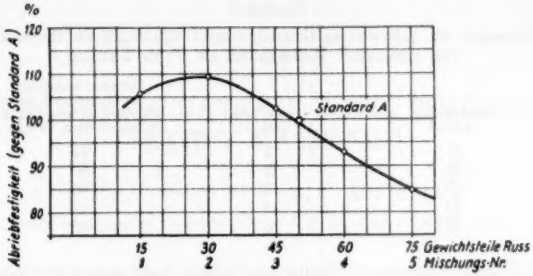

FIG. 6.—Abrasion resistance of a tire-tread compound as a function of the proportion of carbon black added.

Dimensions of test-specimen	10 mm. diameter, 6 mm. thick.
Test load	127 g. per sq. cm.
Emery paper	Silcarbo paper 40, series E 770 Extra.
Time of abrasion	15 minutes.

Ordinate—Abrasion resistance, referred to Standard A
Abscissa—Top values = parts by weight of carbon black
Lower values = Compound No.

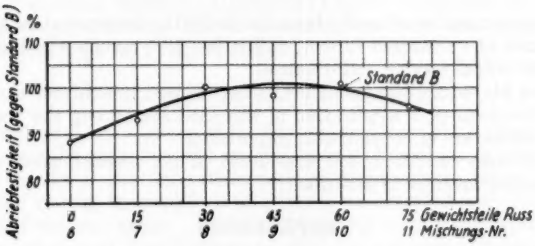

FIG. 7.—Abrasion of a shoe sole compound as a function of the proportion of carbon black added.

Dimensions of test-specimen	10 mm. diameter, 6 mm. thick.
Test load	127 g. per sq. cm.
Emery paper	Silcarbo paper 40, series E 770 Extra.
Time of abrasion	15 minutes.

Ordinate—Abrasion resistance, referred to Standard B.
Abscissa—Top values = parts by weight of carbon black.
Lower values = Compound No.

Here again, under the selected test conditions, there is an optimum at 30 to 60 parts of carbon black by weight (Figure 7).

PRACTICAL EXPERIENCE VERSUS DÄTWYLER–SCHILTKNECHT ABRASION–TESTING MACHINE

In Table 5 below we show a comparison of ratings of abrasion resistance of tire treads in actual service and as indicated by the Dätwyler-Schiltknecht machine. By the heating "In service", we mean the results of years of experience based on reports of salesmen, customers and test drivers.

In this case, then, the agreement is very close. However, it must be assumed that, according as tire treads, shoe soles, or other vulcanized products subject to abrasive wear are to be tested, it will be necessary to arrive at optimum agreement with service performance by trial-and-error variation of test

TABLE 5

SERVICE VS. DÄTWYLER–SCHILTKNECHT MACHINE IN RATING THE ABRASION RESISTANCE OF TIRE TREADS

Compound symbol	In service (rank)	Abrasion resistance in %, referred to Standard A, load 127 g., abrasion time 15 min.
A	1	97
B	2	80
C	3	75
D	4	46
E	5	46

conditions in each instance. These test conditions primarily relate to test load, torque behavior according to the formula

$$\text{Torque} = (P_2b - P_1a)\sin\alpha + (P_2c + P_1c)\cos\alpha$$

and also to the factor of the resilience of the rubber. Other variables are test temperature, kind of emery surface, abrasion velocity, and time of abrasion.

SUMMARY

Of the great number of methods available for the determination of the abrasion resistance of vulcanized rubber, only a few give results which correlate at all well with actual service performance.

The part played by the resilience of the rubber, the correct choice of test load, and the manner of application of this load are among the many testing conditions which are of considerable importance.

Some of these conditions are considered in the present work, and a new abrasion testing machine is described.

REFERENCES

[1] Buist, *Trans. Inst. Rubber Ind.* **26**, 192 (1950).
[2] Buist, *Trans. Inst. Rubber Ind.* **26**, 197 (1950).
[3] Juve, Graves, and Fielding, *India Rubber World* **116**, 208 (1947).
[4] American Society for Testing Materials, ASTM Standards on Rubber Products, 1950, p. 874; British Standards Institution, Methods of Testing Vulcanized Rubber, B.S. 903 (1950), p. 151.
[5] Buist, *Trans. Inst. Rubber Ind.* **25**, 374 (1950).
[6] British Standards Institution, Methods of Testing Rubber, B.S. 903 (1950), p. 151.
[7] Griffith, Storey, Barkley, and McGilvray, *Anal. Chem.* **20**, 837 (1948).
[8] Methods of Testing Vulcanised Rubber, B.S. 903 (1950); British Standards Institution, London, 1950, p. 151.
[9] Parkinson, RUBBER CHEM. & TECHNOL. **17**, 451 (1944).
[10] Buist, Newton, and Thornley, *Trans. Inst. Rubber Ind.* **26**, 288 (1950).
[11] Buist, *India Rubber World* **121**, 180 (1951).
[12] Buist and Williams, *Trans. Inst. Rubber Ind.* **27**, 209 (1951).

RUBBER EVALUATIONS WITH INSTRON TESTING MACHINE *

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Tensile stress-strain testing occupies a preeminent position in any laboratory system of rubber evaluation. For this reason, new developments in equipment or techniques for measuring stress-strain properties which appear applicable for rubber should be of especial interest to rubber technologists. The Instron testing machine[1], although not specifically designed for rubber testing, possesses features which make it very useful in a rubber laboratory. It makes available novel procedures for the testing of rubber which are not only immediately useful, but are instructive for the possible development of improved techniques for rubber stress-strain testing. A number of these procedures are described and illustrative experimental results presented to show the capabilities of equipment of this type for rubber testing.

DESCRIPTION OF TESTING MACHINE

Several technical descriptions of the Instron machine which adequately discuss its principles of operation and general features have been published[1]. To recapitulate briefly, it uses interchangeable resistance strain gauge load cells. The electronic system of amplification permits an extraordinary flexibility in the selection of the load range. For the instrument used in this work, extreme full-scale tension ranges from 2 grams to 5000 pounds were obtainable by the use of four load cells. Compression load cells to cover ranges up to 5000 pounds were also included. Calibration is checked by dead weight load on a low range for each cell. The deflection of the load cell due to the load is usually negligible, but can be corrected for if desired. The load is recorded with a Leeds & Northrup Speedomax recorder, having a response time of approximately 1 second for full-scale deflection. The chart speed can be varied by change gears between extreme values of 0.2 to 50 inches per minute. This provides a corresponding permissible variation in the magnification selected for the deflections of the test-specimen.

The motion of the crosshead which carries the moving jaw is actuated by a servomechanism which accomplishes rapid and accurate positional response and adjustment by the controls. The speed of the crosshead may be varied by change gears in the range from 0.02 to 20 inches per minute. The instrument used in this work has controls to permit automatic cycling of the crosshead between either adjustable extension or load points.

Since the chart moves in synchronization with the crosshead, the elongation for a dumbbell-shaped test-specimen cannot be recorded directly on the chart. The stretch of the narrow portion of the dumbbell must be observed by means

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of a tape and bench marks or by some other device. A manually operated pip circuit, which permits a mark to be made on the record at any desired point, facilitates such work. The controls can be set to return the crosshead automatically to the desired gauge length at a maximum speed of 20 inches per minute. This is a further limitation on the use of the equipment for routine tension testing, compared to machines which permit the crosshead to be disengaged for rapid return.

The Instron jaws are well suited for measurements of rubber at moderate elongations. For higher elongations, conventional jaws for rubber testing of a "follow-up" type are usually necessary to eliminate slipping. Such jaws can be adapted readily to the machine. In fact, the mounting arrangements for the jaws are such as to encourage the design of jaws for special purposes wherever any advantage is to be secured in this way.

The error in the load-weighing system, regardless of the range used, is less than ± 0.5 per cent with respect to the calibration. Under steady state conditions, the error in the crosshead position is less than 0.001 inch. In the case of a suddenly imposed reversal, the error may be larger (0.005 inch) but, due to the speed of recovery of the system, this larger error is of very short duration.

COMPOUNDS USED

For convenience, the recipes of the rubber compounds which were used are collected together in Table I for future reference.

TABLE I

COMPOUND FORMULAS

Ingredient	Compounds used, parts by weight										
	A	B	C	D	E	F	G	H	I	J	K
GR-S 100 (cold rubber)	100						100	100	100	100	100
Smoked sheet		100	100								
GR-S				100	100	100					
Silica (RS-1)											50
Carbon black (EPC)								50			
Carbon black (HAF)	50		50	50	35				50		
Carbon black (SRF)						60			50		
Zinc oxide	3	3	5	5	5	5	3	3	3	3	3
Stearic acid	1.5	1.5	1	1	1	1	1	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.6	1.6	1.6	1.6	1.6
Diphenylguanidine	0.75	0.25	0.25	0.25	0.25	0.25	0.7	0.7	0.7	0.7	0.7
Mercaptobenzothiazole disulfide	0.25	0.75					0.5	0.5	0.5	0.5	0.5
N-Diethyleneoxy-2-benzothiazole sulfene amide			0.75	0.75	0.75	0.75					
Triethanolamine											3

ULTIMATE TENSILE STRENGTH AND ELONGATION

As may be judged from the foregoing remarks, although the Instron tester may be used satisfactorily for tension tests on dumbbell-shaped rubber test-specimens, it does not show up to particular advantage here in comparison with machines which have been especially developed for this one technique. In theory, of course, it does have an advantage in that the load is applied with a constant strain rate. When there are motion and inertia in the load system, the loading conditions are not so well defined.

It is quite feasible to develop an electronic type of extensometer to work with the Instron system. Figure 1 is a block diagram illustrating such an exten-

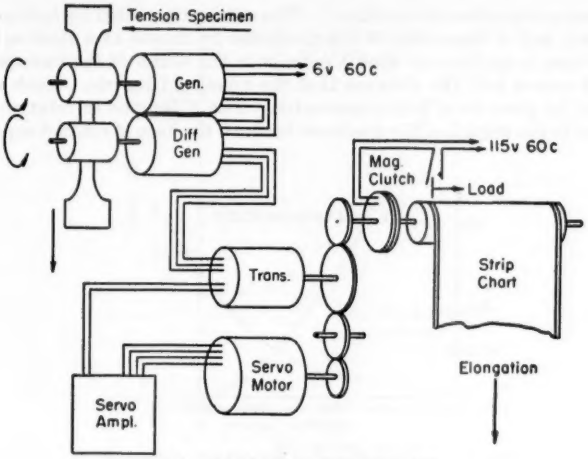

FIG. 1.—Block diagram of extensometer.

someter which has been constructed and found to be suitable for recording the elongation of the straight portion of a rubber dumbbell tension test specimen. Figure 2 is a photograph of the device. It includes a carriage which carries two

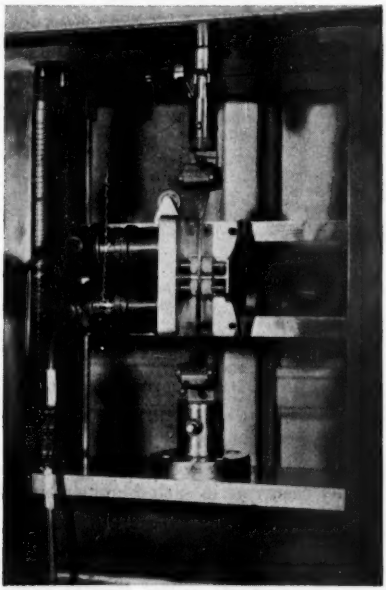

FIG. 2.—Photograph of extensometer.

rollers that contact the test-specimen. The carriage is guided by rods mounted at the rear, and is connected to the crosshead by means of a steel cable and pulley system in such a way that it remains in the center of the test-specimen, that is, it moves half the distance that the crosshead travels. Each roller is connected by gears to a Selsyn generator. The difference in rotation of the rollers due to the stretch of the specimen between the lines of contact supplies an

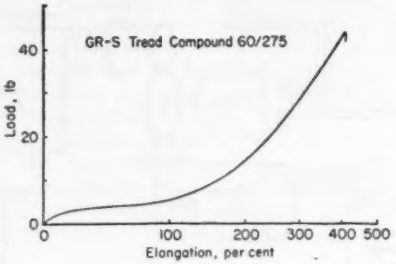

FIG. 3.—Load-elongation curve recorded with extensometer.

error signal by means of an error transformer to a servo-amplifier which controls a servomotor. This drives the chart through a gear system mounted on a bracket on the front of the machine. The motion of the chart nulls the error signal by gear connection to the error transformer.

Figure 3 is a load-elongation curve as recorded with the extensometer. It will be noted that the elongation is recorded in a logarithmic way. This is

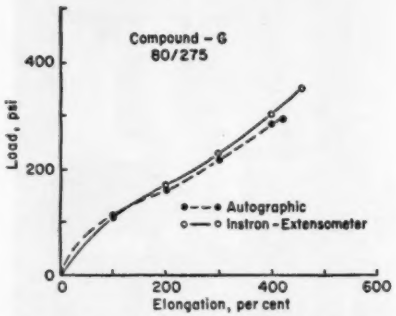

FIG. 4.—Comparison of results for a gum compound.

characteristic of the system. The device records true strain which represents the stretch that is actually occurring in each increment of length of the rubber at any instant. The rubber compound had the same formula as compound A except that hot GR-S was used instead of cold rubber.

Figures 4 and 5 present a comparison of results with the extensometer with those from an Albertoni autographic rubber tension tester. Each curve on these plots is the average curve secured from each of nine test-specimens (three

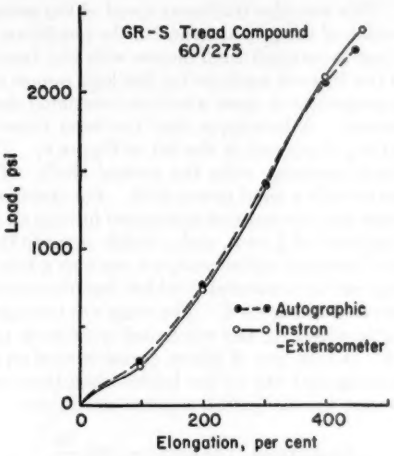

FIG. 5.—Comparison of results for a tread compound.

dumbbells from three test-sheets for each curve plotted). The agreement is considered to be satisfactory. The somewhat higher tensiles and elongations secured with the Instron tester are interesting. The tests were carefully controlled as to temperature, age of test-specimens, etc. The only explanation that seems probable is that this difference is due to characteristics of the machines. For instance, the crosshead speed with the Instron tester was 20

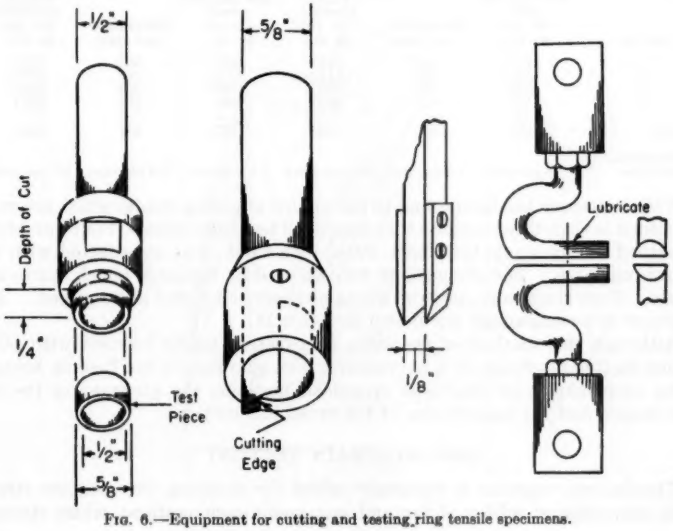

FIG. 6.—Equipment for cutting and testing ring tensile specimens.

inches per minute. This was also the linear speed of the screw of the Albertoni machine, but the motion of the grip attached to the pendulum results in a somewhat lower rate of jaw separation than occurs with the Instron machine.

The accuracy of the Instron machine for low load ranges makes it useful for determining tensile properties in cases where conventional dumbbell test-specimens cannot be secured. A technique that has been found especially useful employs a rotary cutter, illustrated at the left in Figure 6. This is made in two pieces, the outer blade screwing onto the central shaft. The cutter is used either in a drill press or with a hand power drill. For sheets up to $\frac{1}{4}$ inch thick, the cutter will provide ring-shaped test-specimens having an inside diameter of $\frac{1}{2}$ inch, an outside diameter of $\frac{5}{8}$ inch, and a width equal to the thickness of the sheet. For irregularly shaped rubber samples, such as a tire tread, an annular cut about $\frac{1}{4}$ inch deep can be made and a rubber test-ring excised with a special hand tool, also illustrated in Figure 6. The rings are trimmed on a high-speed mandrel with a double edged jig and are tested with hook jaws, illustrated at the right in Figure 6. A thin film of silicon grease is used on the jaws for lubrication. The rubber ring just fits on the hooks when they are together at the start of the test, so that the elongation is given simply by:

$$\text{Elongation (per cent)} = 100\,\frac{2x}{\pi D}$$

where D is the average diameter of the ring, that is, $\frac{9}{16}$ inch, and x is the crosshead travel.

TABLE II

COMPARISON OF RESULTS WITH DUMBBELL AND RING TEST-SPECIMENS

Compound A: Cure, 60 min. at 290° F

	Dumbbells			Rings		
Test no.	300 per cent stress (lb. per sq. in.)	Elongation (per cent)	Tensile strength (lb. per sq. in.)	300 per cent stress (lb. per sq. in.)	Elongation (per cent)	Tensile strength (lb. per sq. in.)
1	1110	525	2430	1035	565	2460
2	1120	490	2140	1100	560	2700
3	1080	525	2560	1085	552	2650
4	1150	575	2800	1053	553	2510
Average	1118	529	2480	1065	557	2580
Average deviation from mean	1.8 per cent	4.3 per cent	8.0 per cent	2.3 per cent	1.0 per cent	3.7 per cent

This technique has been found to be capable of giving results which are more reproducible than those secured with dumbbell test specimens. Four dumbbells were dyed from a single test-sheet, 0.082 inch thick, and were tested with the Instron machine. The elongations were secured by means of bench marks and a scale. Four rings were cut from the same sheet and tested as described. The results of this comparison are shown in Table II.

Although this method of specimen preparation might be used with other tension testing machines, it is particularly well adapted for the Instron because of the coordination of chart and crosshead motions, the accuracy of the low load ranges, and the smoothness of the crosshead motion.

STRESS-STRAIN TESTING

The Instron machine is especially suited for studying the complex stress-strain properties of rubber at low and intermediate elongations, where straight

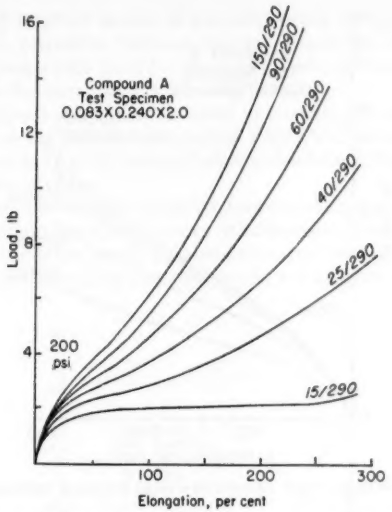

FIG. 7.—Typical load-elongation curves for a range of cures.

strips of rubber can be used with the Instron jaws. The versatility in load range, chart speed, and crosshead motions can then be employed to full advantage for determining the effects of deformation history and other factors on the details of the stress-strain curves. The term stress is used here in the conventional fashion for rubber and is the ratio of the load to the original cross-section.

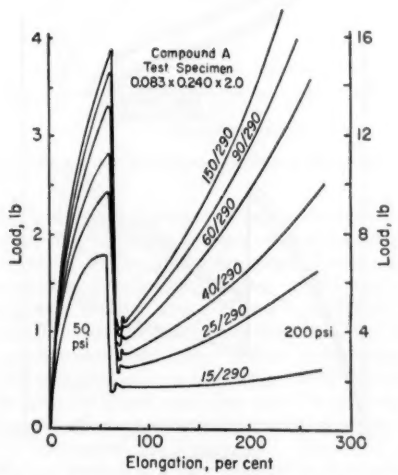

FIG. 8.—Example of the magnification of the load scale for low elongations.

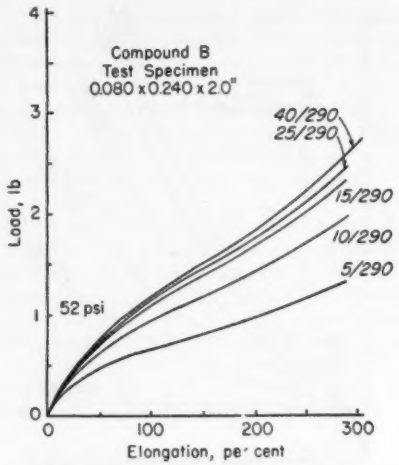

FIG. 9.—Load-elongation curves recorded for a range of cures of Hevea gum compound.

Figure 7 shows stress-strain curves for a series of cures of a cold rubber tread stock, compound A. Figure 8 illustrates how the low elongation portion of these curves can be examined in more detail by starting the curves on a low load range and switching to a higher load range, without stopping the crosshead. The switch in load range was made here to coincide approximately with the inflection point in the stress-strain curves. The change in curvature for the two regions is very pronounced.

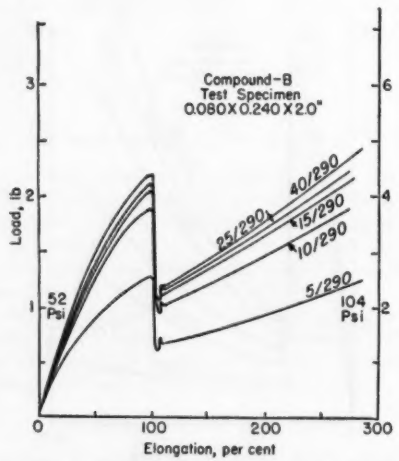

FIG. 10.—Examination of the low elongation region in more detail.

Figures 9 and 10 show results of a similar study for compound B, a Hevea gum stock. The transition between the two directions of curvature is more gradual for the gum stock than for the tread stock, so that the second portion of the curves for the gum stock are nearly linear.

In most applications, rubber is used at relatively low elongations. The ability to examine the stress-strain curves with good accuracy and facility for elongations as low as 10 or 25 per cent adds something hitherto not available for rubber testing laboratories.

The stress-strain curve now in use for rubber evaluation is strictly a transient curve. The large deviation which may exist between the transient stress-strain curve and the equilibrium curve obtained after repeated cycling is illustrated in Figure 11. Since the cycling controls can be set to work automatically, it be-

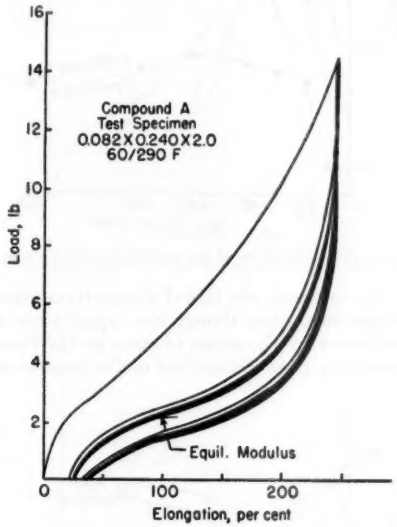

FIG. 11.—Comparison of initial and equilibrium load-elongation curves.

comes feasible, for instance, to request of an operator the modulus for 100 per cent elongation after four cycles to 300 per cent elongation. This information can be secured about as readily as the transient, first-stretch modulus.

Figure 12 shows the divergence between initial and equilibrium 100 per cent modulus values for a GR-S and a Hevea tread stock for a range of cures.

It is known that the deviation between the initial and equilibrium modulus values is most pronounced for tread stocks containing reinforcing carbon blacks. But if the comparison is made using a nonreinforcing black at a high enough loading to give an initial modulus equal to that secured with the reinforcing black, then the effect may be just as large or larger with a "soft" black. This is shown by the curves in Figure 13. Thus this spread between the initial and equilibrium moduli is a very general phenomenon with rubber compounds.

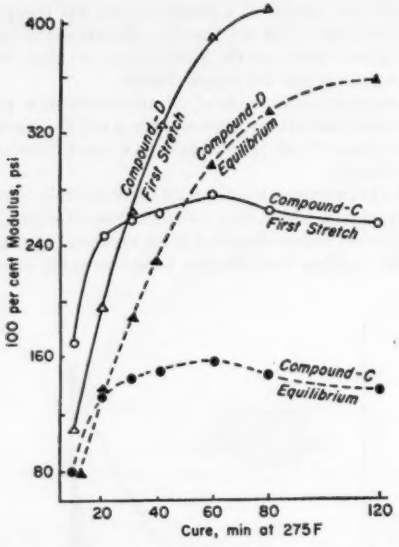

FIG. 12.—Divergence of initial and equilibrium modulus values.

The interesting way in which the initial stress-strain curve tends to be resumed at higher elongations, even though the equilibrium curve obtains for lower elongations, is shown by the series of steps in the stress-strain curve in Figure 14. This curve is a good illustration of the functioning of the manual crosshead controls.

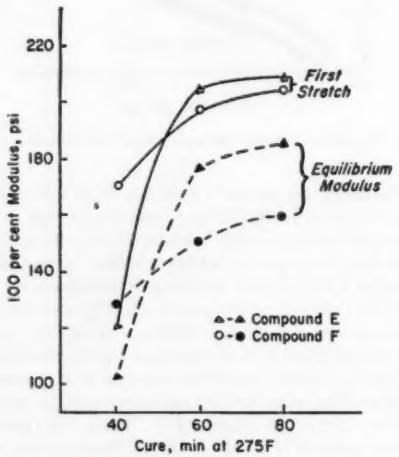

FIG. 13.—Effect of type of black loading on initial and equilibrium modulus.

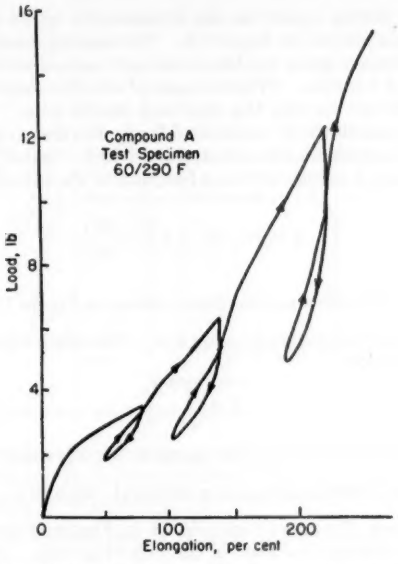

FIG. 14.—Illustration of the functioning of the crosshead controls.

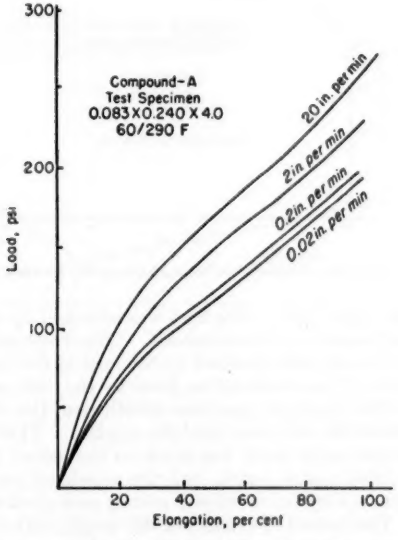

FIG. 15.—Effect of crosshead speed on load elongation curves.

The effect of testing speed on the stress-strain curve of compound A at lower elongations is shown in Figure 15. The testing speeds shown were obtained by using change gears for the crosshead motion with a constant initial specimen length of 4 inches. Wider ranges of effective testing speeds could, of course, be secured by varying the specimen length also. The spread in the curves should be quantitatively accounted for by the creep characteristics of the rubber, using an analysis similar to that described by Nadai[2] for such curves for metals. The stress, s, is regarded as a function of the rate of strain, u, and the strain, ϵ, so that:

$$s = f(\epsilon, u) = f\left(\epsilon, \frac{d\epsilon}{dt}\right)$$

Using a family of curves such as those shown in Figure 15, $\frac{d\epsilon}{dt}$ can be secured as a function of ϵ for any constant value of s. The creep curve for this value of s will then be given by:

$$t = \int_0^{\epsilon} \frac{d\epsilon}{u}$$

This integral can be obtained by graphical integration from a plot of the values of $\frac{1}{u}$ *versus* ϵ corresponding to a constant value of s.

To test the ideas, the creep curve shown in Figure 16 was secured. To do this, the Instron machine was used in the following way. A practice test strip

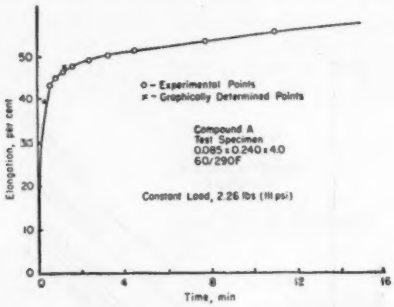

FIG. 16.—Comparison of creep results by two methods.

was clamped in the upper jaw. The load was attached by means of the lower jaw, which was not fastened to the crosshead. The crosshead was then lowered slightly below the lowest point reached by the load in the initial stretch of the piece. The position of the crosshead as given by the dials on the machine was recorded. A new test-specimen was then substituted, the chart started, and a pip mark made when the load was carefully applied. The instant the weight touched the crosshead, a pip mark was made on the record, the time from load application noted from a stop watch, and the crosshead lowered a small step. This procedure was repeated as often and as long as desired to secure points on the creep curve. The instant of contact of the weight with the crosshead could be determined very precisely by the subsidence of the inevitable small oscilla-

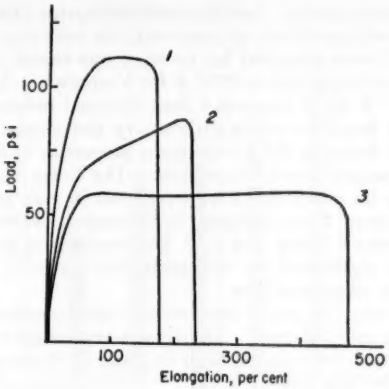

FIG. 17.—Illustration of load-elongation curves for unvulcanized compounds.

tions resulting from room vibrations and air currents, although a sensitive direct load indication could also have been obtained from the chart.

The graphical integration previously described was carried out. The points secured are shown in Figure 16. The form of the ϵ *versus* $\frac{1}{u}$ curve was not conducive to lending high precision to the procedure. Nevertheless, the agreement of the points with the observed creep curve is satisfactory enough to establish a relation between creep and the effect of rate of strain on the stress-strain curves.

The low load ranges and smooth crosshead motion of the Instron machine enable it to be used for measuring the stress-strain characteristics of unvulcan-

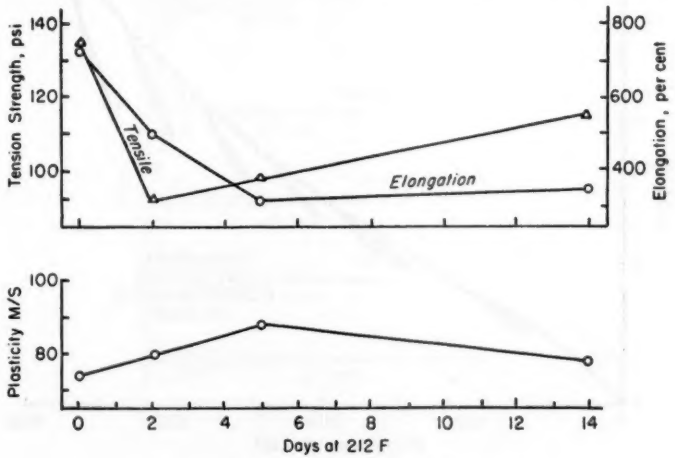

FIG. 18.—Effect of aging on properties of raw polymers.

ized polymers and compounds. In this work, the Instron jaws can be used with straight strips for test-specimens, as jaw breaks do not occur. For tread compounds, test-sheets were prepared by pressing out sheets of the compounds under moderate conditions such as 230° F for 5 minutes. Raw polymers were pressed out at 300° F for 2 hours and then clamped between plates at room temperature for 24 hours to secure satisfactory test sheets. Figure 17 illustrates the diversity found in the stress-strain properties of three experimental oil-polymer unvulcanized tread compounds. The lower modulus and higher ultimate elongation for compound 3 were reflected in very satisfactory factory processing. Compound 2 was marginal in processing, whereas it was impossible to use compound 1 in the factory. The modulus of the raw tread compound is especially significant for evaluating the tendency to pull open the tread splices on raw, expanded tires.

Figure 18 illustrates the use of stress-strain measurements to ascertain the aging stability of a raw polymer. The tensile and elongation measurements appear to be more sensitive to aging than do those of Mooney plasticity, which are generally used for this type of work.

HYSTERESIS DETERMINATIONS

The automatic cycling controls for the crosshead motion enable hysteresis determinations to be made readily by comparison of the areas of equilibrium hysteresis loops with areas under the stress-strain curves. Such data can readily be obtained for different loop amplitudes at various locations on the stress-strain curve. Figure 19 shows a series of loops made in conjunction with the stress-strain curve of a natural-rubber gum stock. Information of this type should be of considerable value from a research standpoint for understand-

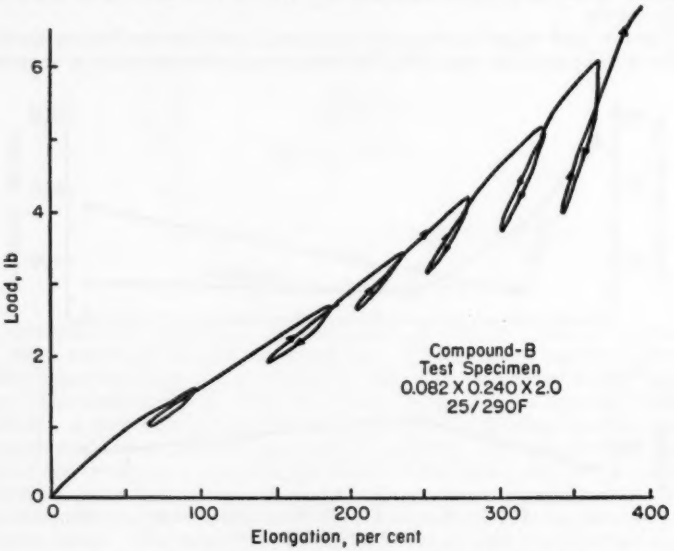

FIG. 19.—Hysteresis loops at various locations on a load-elongation curve.

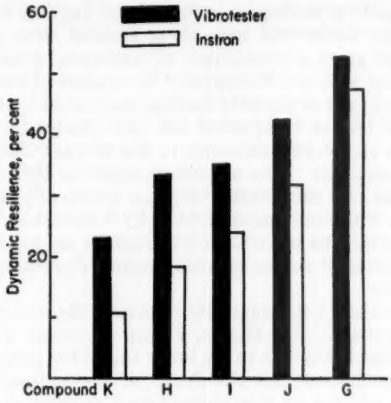

FIG. 20.—Comparison of Instron and Vibrotester resilience values.

ing the nature and structural mechanism of hysteresis losses for elastomers. For laboratory evaluations of hysteresis of direct practical interest for tire service, experience has indicated that low amplitude, high frequency oscillations in shear or compression at a controlled elevated temperature are desirable. It would probably not be worth while to try to substitute Instron hysteresis determinations for those secured with these specialized techniques. Nevertheless, in cases where only tension specimens are available or under similar unusual circumstances, the Instron determinations can be used to advantage. At low

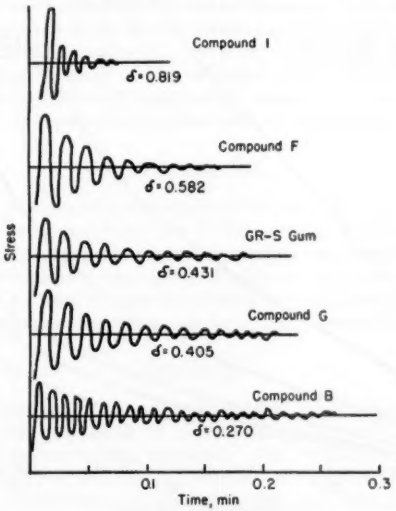

FIG. 21.—Records of free vibrations.

amplitudes, the relative hysteresis ratings from Instron records for various compounds correlate fairly well with those secured from a forced vibration method. Figure 20 gives a comparison of resilience values secured with the Instron machine and with the Vibrotester[3] for a series of five cold rubber compounds, in which the type of pigment loading was varied. It will be noted that the relative ratings for the compounds are very similar for the two methods, although there is a significant difference in the actual values for the resilience given by the two methods. The amplitude cycle for the equilibrium Instron loops was 1 to 10 per cent elongation. A gauge length of 1 inch was used with a test strip specimen with dimensions of 0.082 by 0.24 inch. The frequency was 0.16 cps and, of course, the wave form is essentially square wave. The Vibrotester conditions included sinusoidal compression vibrations of ±1.5 per cent amplitude at 60 cps.

Hysteresis may also be measured by recording the decay of free vibrations with the Instron system. To do this, a strip of rubber was clamped in the upper jaw and a weight attached to the lower end of the strip. The weight was set into vertical oscillation and the decay of the vibratory force recorded. Typical recordings secured by this method for a variety of compounds are reproduced in Figure 21. Although this is an elegant procedure, it does not overcome the inherent disadvantages of free vibration methods. It is, for instance, difficult to secure good precision in the measurement of traces such as those given by the synthetic tread stocks.

COMPRESSION TESTING

The attachments for compression measurements are a valuable adjunct for the Instron machine in a rubber laboratory. The cycling controls and control

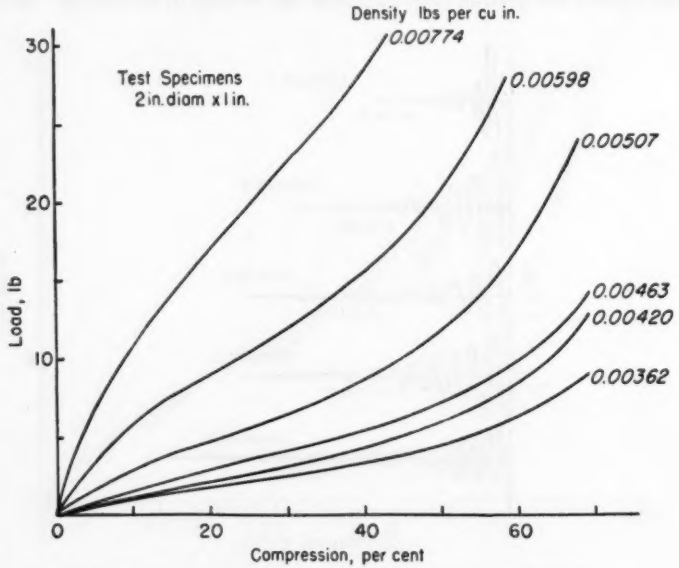

FIG. 22.—Load-compression curves for a series of foamed-rubber specimens.

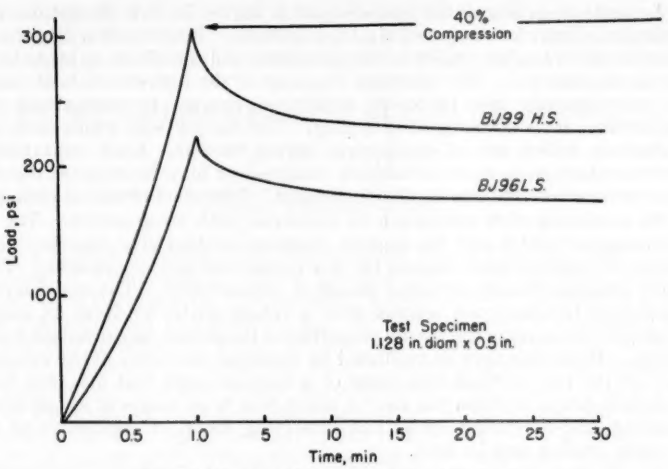

FIG. 23.—Compression loading and relaxation curves.

of the crosshead motions function in the same way as for tensile testing. Two examples will be given from the many applications which occur for laboratory compression testing. Figure 22 shows load-compression curves secured for an experimental series of foamed rubbers of varying density. Figure 23 presents the compression loading and stress relaxation curves secured for two gasket-type rubber compounds[4].

It may be mentioned also that the properties under compressive loading for unvulcanized compounds have shown interesting correlations with the gauge contours of calendered fabrics which, in turn, are related to the plastic and elastic forces causing bending of the calender rolls. Furthermore, the compression system has been readily adapted to secure very precise penetrometer evaluations of the hardness of vulcanized rubber compounds.

CONCLUSIONS

The principles of operation incorporated in the Instron machine give it wide distinctive fields of usefulness in a rubber testing or rubber research laboratory. Its principal limitations for rubber testing are usually associated with unique conditions which occur in rubber testing as contrasted to the testing of other materials. The results available should encourage improvements in the equipment and procedures in general use for rubber stress-strain evaluations.

SYNOPSIS

Results are presented from an investigation undertaken to explore new opportunities for the evaluation of rubber from stress-strain characteristics obtained with an Instron testing machine. The resistance strain gauge load recording system, and the flexibility of control of the crosshead motions introduce a variety of possibilities not available with the usual pendulum type of rubber tester.

Accurate recording of the load-elongation curves for low elongations is of particular interest for many technical applications. Reproducible deformation histories can be applied readily to test-specimens and the effects on load-elongation curves observed. The transient character of the first-stretch load-elongation curve usually used in rubber testing is apparent by comparison with equilibrium curves after repeated cycling. The facility with which such data is obtained makes use of equilibrium curves feasible. Load relaxation at either constant elongation or constant compression may be recorded directly. Creep at constant load can also be determined. The effect of rate of elongation on the load-elongation curves can be correlated with creep curves. The low load ranges available and the smooth crosshead motion give reproducible recording of load-elongation curves for raw rubber and raw compounds. These results have significance for some phases of processibility. The use of a small ring-shaped test-specimen secured with a rotary cutter provides an elegant technique for sampling the tensile properties of the rubber in vulcanized rubber articles. Hysteresis may be evaluated by recording the decay of the vibratory load for the free vertical vibrations of a test-specimen and attached mass. Hysteresis determinations can also be made over large ranges of amplitude by recording load-elongation cycles and measuring areas. Compressive as well as tensile loading may be used.

Results from these various procedures are given to illustrate the versatility and flexibility in testing with this equipment. They indicate important fields of usefulness for it in rubber testing other than routine testing for ultimate elongation and tensile strength, for which it is not particularly well adapted.

ACKNOWLEDGMENT

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REFERENCES

[1] Burr, *Electronics* **22**, 101 (May 1949); Hindman and Burr, *Trans. Am. Soc. Mech. Engrs.* **71**, 789 (1949).
[2] Nadai, "Stephen Timoshenko, 60th Anniversary Volume", Macmillan Co., New York, 1938, p. 155.
[3] Gehman, Woodford, and Stambaugh, *Ind. Eng. Chem.* **33**, 1032 (1941); RUBBER CHEM. & TECHNOL. **14**, 842 (1941).
[4] These two compounds are under study by ASTM Committee D-11, Subcommittee XVII on Tests of Hardness, Set, and Creep.

THE MICROCHEMICAL ANALYSIS OF RUBBER *

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While those who profess to be microchemists have a number of specialized techniques, it is surprising how often microchemistry is used without appreciation that this is being done. As examples in the analysis of rubber, two qualitative color tests may be mentioned that are both applicable to small samples. The first was described by Weber[1] in 1900, but interest in it has been revised recently by Stern[2] and by Parker and Wake[3]. In this test the rubber is treated with bromine and then with phenol; natural rubber gives a violet color and so may be distinguished from synthetic elastomers. In the second test, due to Kirchhof[4], natural rubber is detected by the yellow-to-red color which it gives with trichloroacetic acid. Other reactions carried out with small quantities of rubber for identification purposes include the well known Beilstein test for halogens, in which the organic substance when heated on a copper wire imparts a green color to a Bunsen flame. This method was suggested by Newton[5] for the detection of chloroprenes, and has been applied by Shaw[6] in a systematic procedure for the identification of plastics in general. Spot tests have also been devised[7] that depend on the reactions of the vapors produced by destructive distillation of the rubber being examined; for example, Neoprene gives vapors which bleach paper impregnated with potassium chromate[8], or the density and pH value of the distillate may be determined[9]. The rates of reaction of natural rubber and various synthetic elastomers with mixed nitric and sulfuric acids has been shown[10] to be characteristic and may be determined with small samples. In contrast with the above, some procedures have been called micromethods by their advocates merely because the samples used are smaller than usual. Microchemistry was clearly defined by Emich[11] as covering the range 2 to 10 mg. of substance, and the present author's work described below should properly be termed semimicroanalysis.

In view of the fact that this is a conference of chemists, physical examinations are here mentioned only briefly, although they may provide valuable information and yet consume only small amounts of material. Alber[12] and Wilson[13] have reviewed micromethods for the determination of specific gravity and Wilson[14] those for viscosity measurement: some of these should prove useful in the examination of rubber. It has been said[15] that qualitative information may be obtained by observing the fluorescence of rubber in ultraviolet light; more detailed results are obtainable from an investigation of the ultraviolet absorption spectrum, concerning which reference may be made to two reviews[16]. A recent review[17] of infrared spectrographic methods mentions application to rubber science[18]. The examination of rubber under the microscope has been described by Allen[19], who gives references to the work of other investigators. For the use of the electron microscope, see Ladd[20], Zworykin and Hillier[21], and

* Reprinted from the *Proceedings of the XIth International Congress of Pure and Applied Chemistry* (London), Vol. 5, pages 383–388 (1947). Although the Congress was held in 1947, the Proceedings were not published until 1953.

Kelsey and Hanson[22]. The ultramicroscope has also been used in rubber technology[23].

Particularly during the war years, many papers have been published which describe procedures for the estimation of the dry rubber content of latex, and some of these have been microanalytical methods. Wittenberger and Brice[24] counted rubber particles under the microscope, and other workers[25] have correlated the turbidity of the latex with its rubber content. A more satisfactory method would appear to be that due to Compagnon and Le Conte[26], in which a little latex between microscope slides is coagulated by alcohol.

The author's interest in the microanalysis of rubber arose from the necessity of analyzing a small piece of insulant from a cable, the sample being too small for examination by the classical methods for soft vulcanized rubber; therefore, suitable semimicromethods were devised[27]. Since this work was published, the only investigations on the microanalysis of vulcanized rubber appear to be those of Luke[28] on the semimicrodetermination of total sulfur.

Sampling was one of the problems that required consideration, and it is a subject which is still worthy of rubber chemists' attention. As far as the writer is aware, no one has examined the effect on the analytical results of comminuting the rubber in air (or oxygen) and in an inert gas: until this has been done the effects of fine grinding and local generation of heat cannot be assessed. In preliminary experiments, a single sample was distintegrated in a laboratory roll mill and by rasping. The latter product was considerably finer than the former and it gave an acetone extract of 3.7 per cent, which was not altered appreciably when the fine material was stored in air for three days, whereas the acetone extract of the milled product was 3.4 per cent. The difference between these results could be due either to greater oxidation during the comminution to the finer material, or to failure of the solvent to gain access to the central portions of comparatively large rubber particles. In the writer's laboratory, rubber for analysis on the usual scale is sampled by holding it against a rapidly rotating steel cutting tool, but this procedure is inapplicable to small pieces. It may be possible to comminute the latter by use of a percussion mortar cooled with solid carbon dioxide.

The same apparatus is used for both the acetone and chloroform extractions, and it is modified slightly for the alcoholic potash extraction. It was specially designed for this purpose and can be made in the laboratory, but attention is drawn to a comparison of the performances of various microextractors published by Batt and Alber[29]. The writer's apparatus, as set up for acetone or chloroform extractions, is shown in Figure 1.

The sample is supported on a small sintered glass funnel *B* and is extracted continuously by solvent that drips from the wire frame at the bottom of the condenser *E*; the condensed solvent is guided on to the sample by the funnel *A* and the extract is collected in the capsule *C*, from which the solvent is continuously evaporated. The glass parts with their contents are assembled on the wire frame *G*, and the whole is placed in the glass sample tube *D*, the top edge of which is ground flat so that it is effectively sealed against loss of solvent vapor when the condenser *E* is in position. The frame *H* is convenient for holding the sintered funnel *B* on the balance pan. The condenser is made from brass tubing ($\frac{1}{4}$ inch outside diameter, $\frac{1}{16}$ inch bore) and is completely covered with tin by dipping in the molten metal—the frames *G* and *H* are treated similarly. At first, attempts were made to use a small siphon cup in which the sample was placed in a fluted filter paper (diameter 4.25 cm.) but this procedure was abandoned because of irregular action of the siphon and because of

the difficulty of making and handling a grease-free fluted filter. Six units may be connected in series in a water bath 5 in. × 7½ inches, but the rubber connections must be wired on to the condensers.

For the acetone and chloroform extractions, about 20 mg. of sample is weighed accurately in the sintered funnel and about 3 cc. of solvent is placed in the capsule *C* by means of a small all-glass wash bottle. Experiments have shown that the acetone extraction is completed in about two hours and the chloroform extraction in about 1½ hours. At the end of these periods the frame and its contents are withdrawn from the outer tube; the lower part of the frame and the outside of the capsule are rinsed with solvent, and the washings collected in the outer tube, from which they are transferred to the capsule; the solvent is evaporated from the latter on a warm water bath and this is accelerated by means of a gentle current of filtered air. The capsule is dried finally for 15 minutes at 105° C prior to weighing. [The author's attention has been drawn by W. C. Wake of the Research Association of British Rubber

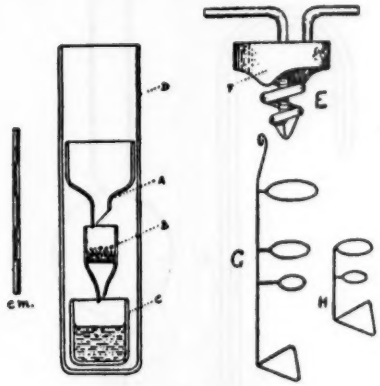

FIG. 1.—Extraction apparatus.

Manufacturers to the fact that some difficulty may be experienced with the microdetermination of an acetone extract, because, in "blanks", a nonvolatile product may be formed, apparently by polymerization of the acetone. The author has not encountered this difficulty, and it has yet to be determined how it can be avoided with certainty.]

After the acetone extraction, there is no necessity to remove all of the solvent from the rubber, but no solvent should remain after extraction with chloroform because the latter would react with the alcoholic potash solution used subsequently. The chloroform is easily removed under reduced pressure. For the alcoholic potash extraction, the rubber is transferred from the filter funnel *B* to an empty outer tube *D* by means of a Pregl's feather[30], and about 1.5 cc. of *N* alcoholic potash solution is measured on to it by means of a pipette. A blank determination is made with the same quantity of potash solution. Absolute alcohol is used and is preferably purified with silver oxide, as described by Stout and Schuette[31] in order to reduce the blank value to a minimum (almost mil). The rubber and alcoholic potash are heated under reflux for 1½ hours, and the extract is filtered through a Pregl cotton-wool filter[32] into

a small beaker. It is evaporated almost to dryness on the water bath, using a gentle current of filtered air, and the residue is dissolved in a little water. The solution is filtered and is drawn by suction into a Browning[23] separatôr (Figure 2), having a bulb capacity of about 10 cc.; a small separatory funnel may be used as an alternative, but is less convenient. In the Browning separator extractions are effected in the bulb and the lower layer is removed via the capillary, which is also used for the introduction of solutions and solvents. The alcoholic potash extract, after transfer to the separator, is acidified with dilute

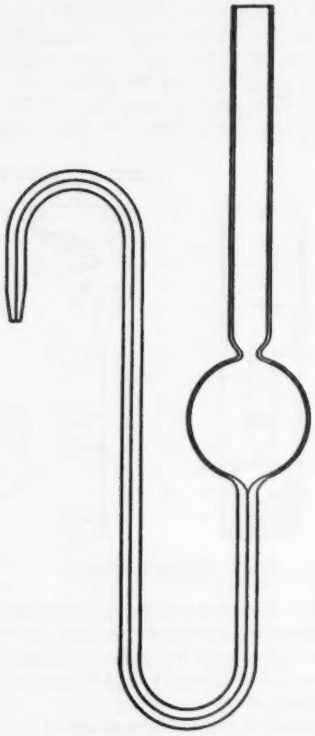

FIG. 2.—Browning separator.

hydrochloric acid and is extracted with two quantities, each of 5 cc., of ether. The ether extract is washed twice with a few cc. of water and is run into a small weighed flask, the separator being washed with a little ether. The ether is removed on the water bath and the flask heated for 15 minutes at 105° C prior to weighing.

The apparatus shown in Figure 3 was devised for the total fillers determination. About 10 to 20 mg. of rubber is weighed accurately into the microbeaker *A*, to which may be attached, by means of a ground joint, the air condenser *B*. The rubber is covered with a layer of α-nitronaphthalene crystals about 1 cm.

deep, and the mixture is heated in an oil bath previously heated to about 200° C. After heating for 15 minutes (longer is required for the decomposition of some samples), the air condenser is removed while the apparatus is still warm. When the microbeaker has cooled, about 4 cc. of benzene is added to the contents. The fillers are allowed to settle and the supernatant solution is removed through a filter-stick; the residual fillers are washed with benzene and the beaker and filter-stick are dried, preferably in a Benedetti-Pichler drying block[34], and weighed together.

In all the above quantitative methods the precautions usual to microchemical analysis must be observed; for example, the wiping technique before weighing the glass vessels. The extraction processes are arbitrary when applied on the usual scale so that it is necessary to make the microextractions in such a

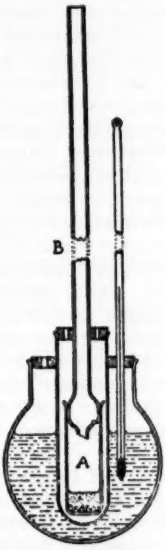

FIG. 3.—Total fillers apparatus.

manner as to yield comparable results: the data supporting the new methods were quoted in the earlier paper[27]. The difficulty of making results obtained on the microscale agree with those from an arbitrary macromethod would need to be surmounted if the wet oxidation of rubber to acetic acid[35] was attempted on small samples, but this problem has not been examined; the older method of calculating the rubber content of the vulcanizate (by difference) was used instead. It was, therefore, necessary to determine the amounts of sulfur present in various forms. Both the microanalytical and rubber literatures have numerous references to the determination of sulfur, and a wide choice of methods is available. Those selected by the author are described briefly and other procedures, probably equally satisfactory, are noted.

The total sulfur was determined[27] by fusion of about 5 mg. of the rubber with sodium peroxide mixed with sodium and potassium carbonates (fusion

mixture). The cooled melt was extracted with hot water, the filtrate was acidified with hydrochloric acid, and was evaporated to dryness to render silica insoluble. The solid was extracted with hydrochloric acid and the sulfate precipitated by barium chloride; the precipitate was collected and weighed in a porcelain micro-Neubauer crucible. The "free" sulfur in the acetone extract was determined by a modification of the bromine oxidation method, in which it was finally precipitated as barium sulfate and was weighed in a procelain micro-Neubauer crucible. The sulfur present in the total fillers may be determined conveniently by a fusion method.

The Carius method of sulfur determination was adapted to microanalysis by Pregl[36], and has been modified by Niederl, Baum, McCoy, and Kuck[36]; it is reliable and is not so hazardous as the classical Carius procedure. For routine analyses Belcher's recommendations[37] should prove useful; he suggests rapid combustion of the sample in oxygen in an "empty" tube as a satisfactory development of the standard microcombustion[38]. For volumetric finishes to combustion methods, reference may be made to papers by Gibson and Caulfield[39], Brewster and Rieman[40], and by Pedersen[41]. Ingenious methods have been devised by Ingram[42] and by Lacourt and Chang[43]. In the former, traces of sulfur are determined by causing the acid gases from a combustion in oxygen to react with copper oxide; and the copper that passes into solution is estimated colorimetrically. Lacourt and Chang absorb the oxides of sulfur, produced by combustion of the sample in oxygen, on metallic silver as in the Pregl carbon-hydrocarbon determination[30], silver sulfate is dissolved from the wire by treatment with ammonia solution and the sulfate is determined as barium sulfate. Routine microdeterminations of organic sulfur are also made by combustion in a bomb[44] and by fusion methods[45]. Sulfur present in the form of sulfide has also been determined by a microevolution process[46].

It may be contended, justifiably, that the various methods at present in use for the determination of traces of copper and manganese in rubber are, in fact, microchemical. In view of recent findings[47] that the combinations in which these elements are present are probably of greater significance than their concentrations, the literature on their methods of determination is not reviewed here.

In conclusion, attention is drawn to an important development in the analytical chemistry of rubber, the application of chromatographic separations. This technique has been used by Bellamy, Lawrie, and Press[48] for the examination of the acetone extract of vulcanized rubber for the identification of accelerators: it was applied qualitatively and on the usual scale, but the quantitative microtechnique has already been established for chromatography in other fields.

ACKNOWLEDGMENT

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REFERENCES

[1] Weber, *Ber.* **33**, 791 (1900).
[2] Stern, *India-Rubber J.* **106**, 449 (1944).
[3] Parker and Wake, *Analyst* **70**, 175 (1946).
[4] Kirchhof, *Kautschuk* **4**, 190 (1928).
[5] Newton, *India-Rubber J.* **107**, 230 (1944).
[6] Shaw, *Ind. Eng. Chem. Anal. Ed.* **16**, 541 (1944).
[7] Burchfield, *Ind. Eng. Chem. Anal. Ed.* **17**, 806 (1945).
[8] Roberts, *Rubber Age & Synthetics* **26**, 22 (1945).
[9] Burchfield, *Ind. Eng. Chem. Anal. Ed.* **16**, 442 (1944).

[10] Parker, *J. Soc. Chem. Ind.* **63**, 378 (1944).
[11] Emich, "Microchemical Laboratory Manual", English translation, John Wiley & Sons, New York, **1932**.
[12] Alber, *Ind. Eng. Chem. Anal. Ed.* **12**, 764 (1940).
[13] Wilson, *Metallurgia* **1946**, p. 157.
[14] Wilson, *Analyst* **71**, 117 (1946).
[15] Radley and Grant, "Fluorescence Analysis in Ultraviolet Light," Chapman and Hall, London, **1939**, Chap. 17.
[16] Jarrijon, *Chim. & ind.* **50**, 34 (1943); Kaye, *India-Rubber J.* 111, 145 (1946).
[17] Thompson, *Annual Rept. of Chem. Soc.* **45**, 5 (1945).
[18] Jarrijon, *Rev. gén. caoutchouc* **20**, 89 (1943).
[19] Allen, *Ind. Eng. Chem. Anal. Ed.* **2**, 311 (1930); **14**, 740 (1942).
[20] Ladd, *Ind. Eng. Chem. Anal. Ed.* **16**, 642 (1944).
[21] Zworykin and Hillier, *J. Colloid Chem.* **6**, 118 (1946).
[22] Kelsey and Hanson, *J. Applied Physics* **17**, 675 (1946).
[23] Hauser and Le Beau, *India-Rubber J.* **110**, 169 (1946).
[24] Wittenberger and Brice, *Ind. Eng. Chem. Anal. Ed.* **18**, 209 (1946).
[25] Navashin and Cherednichenko, *Compt. rend. acad. sci. USSR* **48**, 289 (1945); Traub, U. S. Dept., Agri. *Tech. Bull.* No. 920 (1946).
[26] Compagnon and Le Conte, *Rev. gén. caoutchouc* **21**, 102 (1944).
[27] Wyatt, *Analyst* **66**, 362 (1941).
[28] Luke, *Ind. Eng. Chem. Anal. Ed.* **15**, 602 (1943); **17**, 298 (1945).
[29] Batt and Alber, *Ind. Eng. Chem. Anal. Ed.* **13**, 127 (1941).
[30] Pregl, "Quantitative Organic Microanalysis", English translation, Churchill, London, 2nd Ed., **1930**; Grant, "Quantitative Organic Analysis Microanalysis Based on the Methods of Fritz Pregl", English translation, Churchill, London, 4th Ed., **1945**.
[31] Stout and Schuette, *Ind. Eng. Chem. Anal. Ed.* **5**, 100 (1933).
[32] Pregl, "Quantitative Organic Analysis Microanalysis", English translation, Churchill, London, 2nd Ed., **1930**.
[33] Browning, *Mikrochem.* **26**, 54 (1939).
[34] Benedetti-Pichler, *Mikrochem.* **1929**, Pregl-Fest. 6; "Introduction to the Microtechnique of Inorganic Analysis", John Wiley & Sons, New York, **1942**.
[35] Burger, Donaldson, and Baty, RUBBER CHEM. & TECHNOL. **16**, 660 (1943).
[36] Niederl, Baum, McCoy, and Kuck, *Ind. Eng. Chem. Anal. Ed.* 12, 428 (1940).
[37] Belcher, "Microchemistry and its Applications", Roy. Inst. of Chem., Monograph, **1946**.
[38] See also Schöberl, *Angew. Chem.* **50**, 334 (1937); Belcher and Godbert, "Semimicroquantitative Organic Analysis", Longmans, Green & Co., London, **1945**.
[39] Gibson and Caulfield, *Analyst* **60**, 522 (1935).
[40] Brewster and Rieman, *Ind. Eng. Chem. Anal. Ed.* **14**, 820 (1942).
[41] Pedersen, *Dansk. Tids Farm.* **18**, 1 (1944).
[42] Ingram, *Analyst* **70**, 423 (1945).
[43] Lacourt and Chang, *Bull. soc. chim. belg.* **50**, 115, 135 (1941).
[44] Elek and Hill, *J. Am. Chem. Soc.* **55**, 2550 (1933).
[45] Emerson, *J. Am. Chem. Soc.* **52**, 1291 (1930).
[46] Klinger, Kock, and Blaschezyk, *Angew. Chem.* **53**, 537 (1940).
[47] Morley, *J. Rubber Research* **16**, 31 (1947); Research Association of British Rubber Manufacturers, *J. Rubber Research* **16**, 33 (1947).
[48] Bellamy, Lawrie, and Press, *Trans. Inst. Rubber Ind.* **22**, 308 (1947).

RELATION BETWEEN STRESS RELAXATION AND AGING RESISTANCE OF RUBBER VULCANIZATES. II. EFFECT OF COPPER IN VARIOUS ACCELERATED STOCKS *

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INTRODUCTION

As was shown in a previous paper[1], a definite relation exists between aging and relaxation rates for rubber vulcanizates. Gee[2] has shown that the modulus of stocks with the same "compound" viscosity determines the average molecular weight between bonded units. We shall, therefore, expect to find a constant sulfur-bond distribution in related vulcanizates with the same niveau of moduli and Mooney plasticity and, hence, the same free energy for the process of oxidation. If various retarding agents such as antioxidants are added, measurement of the rate of relaxation of the stress at constant elongation will conform with the rate of aging expressed in terms of tensile strengths.

For vulcanizates with the same system of accelerators but containing different fillers, the moduli will vary widely, and interpretation of the stress relaxation measurements (abbrev. SR) will become difficult. The same will hold for systems with boosted accelerator complexes. Plain accelerator/sulfur stocks seem, on the contrary, to give approximately the same range of stability whether tested in aging or relaxation.

Thus the merit of the relaxation method is the rapid evaluation of the catalytic effect of compounds which does not interfere with the state of cure. By a proper choice of the temperature, the SR measurement can be completed in minutes, and it is possible to select the active compounds for the more tedious control in aging.

Especially for work with the antioxidant effect in thiuram vulcanizates without addition of sulfur where the shelf aging in air at 95° C lasts for 50–60 days, the use of the stress relaxations measurement at temperatures of 130–150° C represents a very convenient method of information. The copper effect described in the following was actually stated with the SR method. Since the method easily might be conducted half or fully automatically, it is very suited for research work or even for control.

METHOD

THE FIRESTONE BALANCE

The Firestone balance previously described[1] was slightly altered in the course of the work. For convenience, the balance was placed outside, on the top of the thermostat. This greatly facilitated the changing of the load (see Figure 1). The contact signaling the equilibrium point was made from a 20 × 0.5 mm. platinum wire (*e*) dipping in mercury covered with glycerol (*f*).

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This system invariably worked successfully in the many measurements carried out. The upper roller for the test ring was placed so that it revolved easily on two pin screws in order further to equalize the strain. In later work (not described in this paper) the heating lamps in the thermostat were replaced by a modified "decade" heater with nichrome wires wound on Eternite plates in 2×500, 2×200, 100 and 50-watt units.

Two 200-watt elements were wound in coils suspended freely in the air for the heat-capacity-free automatic temperature control affected with the contact

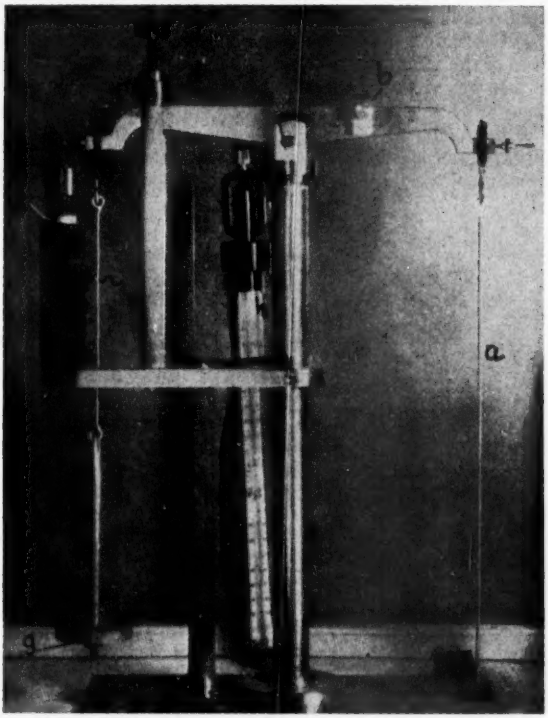

FIG. 1.

thermometer (h). All terminals from the heaters were centralized on a panel with an ammeter showing the total heating current and with a switch for each heater. Finally, the asbestos insulation of the oven was increased to 30 mm. and, by balancing the heating current, a temperature stability was reached with a temperature variation of less than $\pm 0.1°$ C at the middle of the strained sample and a difference of about 1° C between the lower and upper rollers.

The measurements might be started immediately after inserting the ring, which should be done quickly. The measurements were carried out with rings 0.85–0.90 mm. thick. The modulus at constant 170 per cent elongation at

6 seconds' time is obtained by interpolation from the load-log time graph. The time (t_4) for the passage of 50 per cent of the load at 6 seconds was recorded automatically by means of a synchronized watch stopped by an auxiliary relay with impulse from the main signalling system.

DUMBBELL AND AGING

Figure 2 shows a new dumbbell type as used in the aging tests. The concave portions of the outline take the form of arcs of circles. This pattern is referred to below as NKT. The samples were placed on aluminum plates with slits so arranged that there was an air gap around the narrow part of the dumbbell. At 70° C a simple propeller was used for circulating, and for the test at 95° C an oven of the same type as the relaxation oven was used. The temperature in this case was virtually constant throughout the oven, and the temperature variation was less than ±0.1° C. The variation at 70° C was ±0.5° C.

From the aging curve (TB-time) a t_4 value for the tensile strengths is computed chiefly by interpolation between two values neighboring the 50 per cent value of the original tensile. According to the shape of the curve, the interpo-

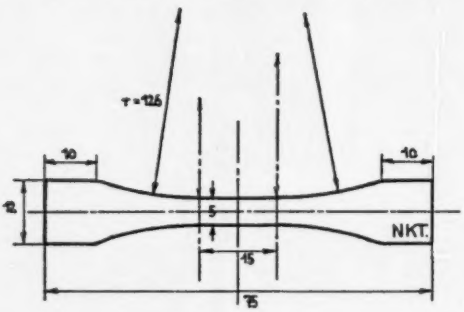

FIG. 2.

lation in some cases was done graphically. All measurements were conducted with 2-mm. thick dumbbell NKT, except the 5211-14 stocks, which were tested as 1-mm. thick specimens.

RATE OF OXIDATION

The rate was determined manometrically, using a modified Dufraisse method[3]. The waste from the cutting of the test ring for the SR was used. No grinding was performed, in order to avoid introduction of impurities or excessive work, as recommended by Stafford and van Amerongen[4]. The values refer to an oxygen pressure of about 650 mm. Hg, and are expressed as moles O_2 per hour and gram C_5H_8, omitting the factor 10^{-8}.

Stocks

The compounds representing four characteristic types of acceleration were prepared from a common batch having the following composition:

Smoked sheet EE 1X	100
Stearic acid	1
Zinc oxide	10
Washed whiting (Danish)	106.5

Standard portions of the batch were weighed, and the following amounts of accelerators and sulfur were added on a mill:

(1) Santocure stock: 1 part accelerator, 1 S.
(2) Boosted thiazole stock: 1.5 part MBT, 0.5 DPG, 1 S.
(3) Low-sulfur thiuram stock: 2 parts TMT, 0.3 S.
(4) Sulfur-free thiuram stock: 2 parts TMT.

Santocure, MBT, and DPG from Monsanto, TMT from Sharples. "Part" means parts per hundred rubber (PHR).

The addition of antioxidants and copper (as copper stearate with 10.4 per cent copper) is listed in Tables I to III.

Measurements

Santocure Stocks.—The vulcanizates containing copper all had a faint greenish tint, indicating that no reaction with the accelerator took place. This was expected, as Santocure has the thiol group blocked with cyclohexylamine and, therefore, no capacity for the formation of copper salts. From Table I it is

TABLE I

DATA FOR SANTOCURE STOCKS[a]

No.	Copper (PHR)	Flectol-H (PHR)	$t_{\frac{1}{2}}$ Aging at 70° (days)	$t_{\frac{1}{2}}$ Relaxation at 121° (min.)
51 241	Nil	Nil	57	18.2
242	0.0095	Nil	30	15.6
243	0.055	Nil	18	12.5
51 246	Nil	2	182	95
247	0.013	2	63	83
248	0.0665	2	30	62

[a] Samples cured for 6 minutes at 162° C.
[b] Flectol-H (Monsanto) condensation product of acetone and aniline.

seen that aging at 70° C represents the most sensitive measure of the copper inhibition. The relaxation times, however, clearly indicate the effect too. The maximal effect is given as the time ratios for 51 246/243 as:

Aging at 70° C	about 10 units
Relaxation at 121° C	about 7.6 units

It is further interesting to note the shape of the aging curves for tensile strengths where compounds 51 247 and 248 containing both antioxidant and copper show a period of induction. Next, there is a clear difference between

TABLE II

DATA FOR MBT–DPG STOCKS[a]

No.	Copper (PHR)	Flectol-H (PHR)	$t_{\frac{1}{2}}$ Aging at 70°, days	$t_{\frac{1}{2}}$ Relaxation at 121° C, min.
51 249	Nil	Nil	35	20.5
250	0.050	Nil	34	17.40
251	Nil	2	83	63
252	0.050	2	58	69

[a] Cure: 3 minutes at 152° C.

protected and unprotected stocks, indicating the difference in chain mechanism for the process. Stocks 51 241, 242 and 243 have similar curves, showing only different and increasing strengths of the prooxygenic function.

Boosted Thiazole Stocks.—For the boosted thiazole systems, copper sensitivity is low in the concentration used, certainly due to the ability of the MBT for the formation of copper mercaptides. The stocks, however, show no discolor-

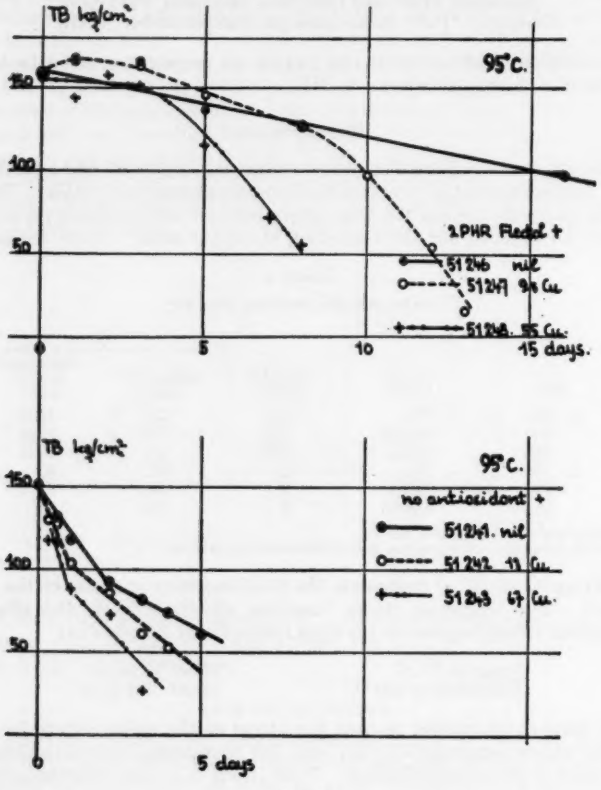

FIG. 3.

ation, but remained faint greenish, as do the Santocure stocks. It is seen that the SR times, especially, are almost unaffected by the copper addition.

Thiuram Stocks.—During compounding of the copper stearate, a notabel color change took place. When the copper stearate had dispersed, ordinarily after 2–3 minutes' milling at 60° C, the color of the batch turned to a distinct brown tone, which deepened on vulcanization. The color was first ascribed to the formation of copper dimethyldithiocarbamate (CuDC), but the analysis of the isooctane extract of, *e.g.*, 5212 with the Beckman photometer showed only a slight displacement of the absorption maximum for zinc dimethyldithio-

carbamate (ZDC) toward the maximum of CuDC. (Absorption maxima are for ZDC at 258 mμ and for CuDC at 270 mμ in 10^{-5} molar solutions in isooctane.) As pointed out by Jarrijon[5], ZDC is the normal reaction product in vulcanizates containing tetramethylthiuram disulfide and zinc oxide, and the 75 per cent yield of ZDC was verified through the extinction values.

If TMT is heated at the boiling point of isooctane (116° C) with copper stearate, the green color turns deep brown. After cooling, a dark precipitate is deposited, leaving a clear supernatant liquid, whereas the yellow solution of CuDC is stable for several days.

TABLE III

DATA FOR THIURAM, LOW-SULFUR STOCKS[a]

No.	Copper (PHR)	Flectol-H (PHR)	Aging at 95° C (days)	Relaxation at 150° C (min.)	Oxidation rate at 121° C (mole $O_2 \times 10^9$)
51 253	Nil	Nil	5.4[b]	7.1	14,300
254	0.050	Nil	13.9[b]	62	3,300
51 255	Nil	2	(41[b])	38[b]	2,600
256	0.050	2	51[b]	90	2,170

[a] Cure: 4 minutes at 162° C.
[b] Value obtained graphically.

The soluble copper in 52 12 (vulcanized) was determined by incineration of the acetone extract and polarographing in ammoniacal solution with Tylose as depressing agent. It was found that one-third of the copper remained soluble. The description of the copper transformations is thus complicated, and a more detailed investigation remains.

We tried, further, to vulcanize a pure-gum stock containing only TMT and copper stearate. The brown color was actually developed, but in the absence of zinc oxide, the vulcanizate was extremely poor. The isooctane extract

TABLE IV

DATA FOR SULFUR-FREE THIURAM STOCKS[a]

No.	Copper (PHR)	Flectol-H (PHR)	Aging at 95° C (days)	Relaxation at 131° C (min.)	Oxidation rate at 119° C (mole $O_2 \times 10^9$)
52 11	Nil	Nil	14.9	80	3790
12	0.050	Nil	32[b]	349	1810
52 13	Nil	2	38.5	378	1310
14	0.050	2	53	537	1010

[a] Cure: 12 minutes at 162° C.
[b] Value obtained graphically.

showed only the presence of excessive amounts of TMT; no further information regarding the colored copper complex was obtained by this procedure.

Tables III and IV show the prominent effect of the copper. Particularly from the decrease of rate of oxidation, it is seen that the copper exerts a true antioxygenic function, and 0.02–0.05 per cent Cu gives the same protection as 2PHR of the very active antioxidant Flectol-H. The factors of retardation are not quite identical, but it is seen that the figures for aging, relaxation, and rate of oxidation qualitatively give the same evaluation of the stability of the thiuram vulcanizates. The retarding function of the copper might be calculated

as the ratios of relaxation times for 51 253/254 and 52 11/12, which gives the values of retardation of 4 and 8 units, respectively.

The function of copper observed here seems to be an interesting example of Dufraisse's "inverse catalysis"[6], according to which most catalysts of autoxidation might shift from pro- to antioxidants, depending on the milieu, etc.

We might finally conclude that copper stearate and TMT form a colored complex having a strong chain-breaking capacity.

SYNOPSIS

Some details for the construction of a modulus balance and thermostat are discussed. A new dumbbell type was developed for aging tests. In four stocks containing different accelerators, the function of copper applied as stearate was investigated. In the case of Santocure, a comparatively high sensitivity was found, and the t_4 (TB) value for aging at 70° C represents a sensitive measure of the prooxygenic effect, whereas relaxation times at 121° C showed a smaller but definite variation. With MBT boosted with DPG, only a limited effect was observed. Conversely, for the thiurams, copper addition produced a marked antioxidant effect, comparable with the retardation normally effected by 2PHR of ordinary antioxidants. 0.05 per cent copper showed an antioxidant activity equivalent to the 2PHR antioxidant. Consistent results were obtained for aging, relaxation, and rate of oxidation. The factors of retardation, as might be expected, however, are not quite comparable. The factor of retardation for copper alone is 4–8 units. The copper develops in the thiuram vulcanizates a strong brown color, giving colored solutions on extraction with acetone and isooctane. As the spectrophotometric determination of the colored complex is difficult, owing to the presence of the strong absorbing ZDC, the nature of the colored complex has not yet been ascertained, but it must somehow be responsible for the inverted action of copper found here.

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REFERENCES

[1] Pedersen and Nielsen, *J. Polymer Sci.* **7**, 97 (1951).
[2] Fletcher, Gee, and Morrell, *Trans. Inst. Rubber Ind.* **28**, 85 (1952).
[3] Pedersen, *Acta Chem. Scan.* **4**, 487 (1950); RUBBER CHEM. & TECHNOL. **24**, 18 (1951).
[4] Van Amerongen, *Medd. Rubber-Stichting*, No. 39 (1944); Stafford, R. L., Imperial Chemical Industries, Ltd., Manchester, private communication.
[5] Jarrijon, *Rev. gén. caoutchouc* **20**, 155, 177 (1943).
[6] Dufraisse, Traité de Grignard: "Catalyse d'Autoxydation", 1936, p. 1157.

THE DISSOLUTION OF VULCANIZED RUBBERS AND ITS BEARING ON PROBLEMS OF RUBBER ANALYSIS *

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INTRODUCTION

Dissolution of a sample of vulcanized rubber is a necessary preliminary to several analytical procedures, e.g., the determination of iodine value or total fillers[2]. If an infallible and convenient agent were available for this process, then doubtless other analytical procedures would be possible of development or improvement and examination of infrared transmission spectra of vulcanized samples would prove a feasible means of identification. Although decalin and nitrobenzene have been widely and satisfactorily used for natural rubber (polyisoprene), there have been several references in the literature to difficulties encountered with the most widely used synthetic rubber, GR-S. Devices to overcome these difficulties include comminution on a roller mill, swelling the sample in strong swelling agents before transferring to the solvent to be used for the dissolution, and grinding on a rubber mill with a plasticizer. All these must be regarded as being of the nature of palliatives, knowledge of the nature of the dissolution process being the real need before the best condition for carrying it out can be decided on. It is shown in this paper that the process is essentially oxidative in nature and, provided that the solvent and rubber are miscible at the temperature of the dissolution, temperature and efficient aeration are the most important rate-determining factors. The nature of the solvent is, of course, of importance with respect to the analytic procedure attempted as all solvents are not suitable for iodine value determination.

THE RATE OF DISSOLUTION IN VARIOUS SOLVENTS

The rate of dissolution was measured by heating the samples, cut into small cubes of about 1 to 2 mm. side with an excess of the solvent for fixed periods of time, and then recovering the samples, extracting them with acetone to remove the high boiling-point solvent, and then drying, the loss in dry weight before and after giving the desired information. The samples were ordinary vulcanized compounds of commerce, and contained, among other compounding ingredients, about 50 parts by weight of carbon black on 100 parts of the rubber. The apparatus used consisted of large boiling tubes 7 by 1½ inches, 3 inches of which were immersed initially in an electrically heated oil bath with thermostatic control at suitable temperatures, recorded later. Later it was found necessary to use gas heating, and control was provided by a regulator of the usual type, but filled with a silicone fluid as the temperature range required (150° to 173° C) was too high for toluene. It may be noted in passing that this regulator was entirely satisfactory in use when once the silicone fluid had been

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degassed. The tubes were closed with a cork carrying a gas inlet tube and an air condenser. About 70 cc. of the high-boiling solvent were used and 0.2 gram of the rubber. Excess of air was provided by passing through the liquid a brisk stream, the rate of which was adjusted by reference to a bubbler tube containing the same solvent as that being investigated, except in the case of *p*-dichlorobenzene, when a saturated solution of calcium chloride was used followed by a drying tube of solid anhydrous calcium chloride. The flow of the air stream was adjusted to be the same in all cases, but the actual rate of flow was not measured. It was, however, of the order of 0.25 liters per minute. In the initial stages of dissolution there is no loss of fillers (carbon black is very easily seen dispersed in solvent, even when present in amounts which are analytically negligible).

There are two ways in which dissolution of samples of the size used could occur. The dissolution could proceed at the interface, in which case, for a constant rate of penetration from each of the surfaces, the loss of volume is

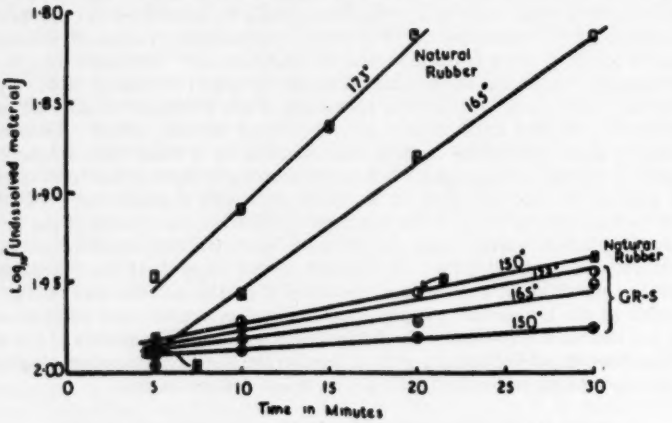

FIG. 1.

directly proportional to the time if the rate of penetration is small and if second-order small quantities are neglected. The dissolution could also proceed throughout the mass of the cube, which becomes highly swollen within a minute of being in the hot solvent. In this case we might expect the reaction to be unimolecular with respect to the polymer. The latter is actually the interpretation used, since losses by weight of up to 10 and 15 per cent of polymer can occur before any dispersion of carbon black is detectable; and if the log of the weight of polymer remaining undissolved at any instant is plotted against time, a linear relationship is obtained in almost all cases until carbon black begins to be dispersed when, of course, the curve swings completely away from linearity. If the surface area played any large part in rate determination then, if for a total weight of W there are n similar particles, the area available will be proportional to $n^{\frac{1}{3}} \times W^{\frac{1}{3}}$. In all cases the number of particles used, as well as the weight, were recorded, and it was found that correction of loss rates to a standard area did not reduce the spread of experimental points. Undoubtedly with considerably larger particles, either attack from the outer zones, or else rate of

diffusion of dissolved polymer from the center of the swollen mass would prove a rate-determining factor, but the evidence indicates that it could be neglected in interpreting these experiments. Figure 1 shows a typical log plot of results obtained, in this case for natural rubber and for GR-S in *p*-dichlorobenzene.

The work started with an examination of the dissolution of GR-S in *p*-dichlorobenzene, since this solvent is recommended for the purpose[1] in order to permit subsequent determination of iodine value as a method for estimating GR-S rubber in vulcanizates. Complete dissolution of GR-S occurred in about 1 to 2 hours, dispersion of black being noticeable after about 40 minutes. These experiments were repeated in a stream of oxygen-free nitrogen instead of air, and no dissolution was apparent after 2½ hours heating at 180° C. With decalin as solvent and oxygen-free nitrogen, 1 per cent was dissolved in 2½ hours, whereas with air dissolution is almost complete in ½ hour. It may be noted here that the rubbers were not degassed, and there is room for doubt as to whether all traces of oxygen had been removed from the nitrogen. Experiments with nitrobenzene were less satisfactory because of this uncertainty, and time has not permitted their replication. It is apparent, however, that, for dissolution at appreciable rates, oxygen is needed. The rate constants cal-

TABLE 1

RATE CONSTANTS FOR THE DISSOLUTION PROCESS

Rubber	Temp.	*p*-Dichlorobenzene	Nitrobenzene	Decalin	*p*-Cymene	α-Nitronaphthalene
Natural rubber	150°	0.75 × 10^{-4}	2.25 × 10^{-4}	0.31 × 10^{-4}	1.5 × 10^{-4}	1.2 × 10^{-4}
	165°	2.7 × 10^{-4}	5.2 × 10^{-4}	0.62 × 10^{-4}		
	173°	3.55 × 10^{-4}	9.6 × 10^{-4}			
GR-S	150°	2.6 × 10^{-5}	0.50 × 10^{-4}	—	5.4 × 10^{-5}	1.5 × 10^{-5}
	165°	5.1 × 10^{-5}	1.4 × 10^{-4}			
	173°	6.8 × 10^{-5}	1.7 × 10^{-4}			
Butyl rubber (GR-I)	150°	0.77 × 10^{-5}	1.0 × 10^{-5}	—	0.4 × 10^{-5}	—
	165°	1.3 × 10^{-5}	1.4 × 10^{-5}			
	173°	1.5 × 10^{-5}	1.4 × 10^{-5}			

culated as for a pseudo-unimolecular reaction for the initial stages of the dissolution, i.e., the linear parts of the curves, are given in Table 1.

It is immediately seen that the rate of dissolution of a given rubber is only varied by a factor of a few units in the change from one solvent to another, but there are changes of ten-fold and more between one rubber and another in the same solvent.

HEAT OF DISSOLUTION

Figure 2 shows the log (rate constant of dissolution) plotted against the reciprocal of the absolute temperature. With the exception of natural rubber in decalin, the plots are reasonably linear, and it is possible to estimate the heat of dissolution from the graphs. It is emphasized, however, that experimental accuracy and the number of points on the curves are insufficient to calculate properly the heat of dissolution, and the figures are offered to assist qualitative discussion only. They are indicated in the diagram.

The overall energy of activation as measured reflects the overall effect of the several reactions that are included in the terms, oxidation and chain scission. Other terms which might be included are either constant or negligible, or may be included as part of the sum total of the oxidative process. The heat of mix-

ing of polymer and solvent is proportional to V_r^2, where V_r is the volume fraction of the rubber and may be ignored, since, for complete dissolution, there is only 0.2 gram of rubber dissolved in 70 cc. of solvent, the volume fraction of rubber being very small. There is evidence that the heats of solution of oxygen in the solvents do not differ appreciably[3] and, in any case, the volume fraction will be small. This, of course, will not apply to solvents such as decalin and *p*-cymene, which form peroxides. In these cases, such reaction of oxygen and solvent, if it influences the dissolution reaction at all, will form part of the series of oxidative reactions leading to chain scission. It is noteworthy that the

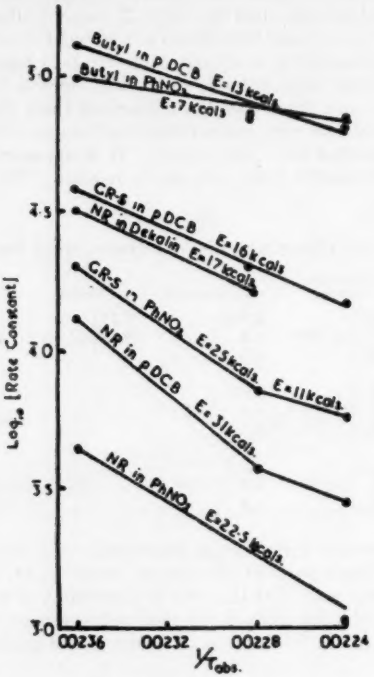

FIG. 2.

slower reactions have, in general, lower activation energies, and this of itself points to complexity of the process.

INTERACTION OF POLYMER AND SOLVENT

Although the volume fraction of rubber is sufficiently small for the heat of mixing of polymer and solvent to be ignored, it does not follow that the solvent plays little or no part in the process. There are two conditions involving the polymer and solvent. The first is that they must be miscible at the temperature of the dissolution; and the second that the vulcanized polymer must be sufficiently swollen in the solvent to facilitate the inward diffusion of oxygen

and the outward diffusion of dissolved polymer. It is also preferable that solvent and polymer are miscible at room temperature, although this is not essential, since a second solvent of lower boiling point can be added during the cooling. This is done, in fact, with *p*-dichlorobenzene, which solidifies above room temperatures.

We may now consider how the two necessary conditions are fulfilled in the solvents investigated.

It has been shown[4] that the heat of solution of a rubber may be regarded as the heat of two liquids, which is given by:

$$H_0 = kV_0\left[\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_1}{V_1}}\right]^2(1 - v_0)^2$$

where the subscripts refer to the two liquids or to liquid and rubber; V is the molar volume; E is the energy of evaporation, the combination E/V usually being referred to as the "cohesive energy density", which can be estimated for rubbers, although the constituents E and V cannot. V_0 is the volume fraction (of solvent) and k is a constant which we may take as being of the order of unity. The heats of mixing of rubber and solvent calculated from this are given in Table 2 for these systems where the dissolution data are complete. They may be taken as sufficiently good to indicate the relative position of the rubbers

TABLE 2

CALCULATED VALUES OF $\frac{\Delta H_0}{(1 - v_0)^2}$

	p-Dichlorobenzene	Nitrobenzene	Decalin
Natural rubber	2.9	0.2	0
GR-S	1.8	0.5	—
Butyl rubber	2.3	0.7	—

with respect to a given solvent, but not as between solvents, since no correcting term has been incorporated for the polar groups of *p*-dichlorobenzene, nitrobenzene, etc.

With the exception of natural rubber and decalin, all systems in Table 2 show positive heats of solution, suggesting that there is a limited solubility and a temperature below which the two components separate as two phases. In the case of Butyl rubber and nitrobenzene, this temperature is well above room temperature, and points to the desirability of using other solvents for this rubber, even if rubber and solvent are miscible at the temperature of dissolution.

The swelling of the vulcanized polymer, before dissolution has occurred, is a function of an expression similar to that for the heat of mixing and is actually a maximum as $\left[\sqrt{\frac{E_0}{V_0}} - \sqrt{\frac{E_r}{V_r}}\right]$ approaches zero. It follows that swelling is a function which varies inversely to the figures in Table 2. It may also be noted at this point that swelling increases as dissolution proceeds, as of course, is expected as chain scission occurs. Swelling, as a percentage increase in weight, is recorded in Table 3 at 173° C and at room temperature for those solvents liquid at room temperature. The figures given are the means of duplicate results rounded to the nearest 5 per cent. The values were obtained after three minutes at the high temperature and are calculated on the weight of polymer remaining at the end of this period.

TABLE 3

SWELLING OF VULCANIZED RUBBERS IN DISSOLUTION SOLVENTS

Rubber	Temp.	p-Dichloro-benzene	Nitro-benzene	Temp.	p-Cymene	Decalin
Natural	173° C	210	160	150°	140	155
Natural	room	—	125	room	140	150
GR-S	173° C	220	170	150°	120	—
GR-S	room	—	125	room	120	—
Butyl	173° C	280	55	150°	85	—
Butyl	room	—	25	room	80	—

Comparison of this table with Table 1 shows that there is no direct correlation between swelling and rate of dissolution. The point will be returned to later in the next section of this paper.

THE GENERAL THEORY OF DISSOLUTION OF VULCANIZED RUBBERS

A theory has been advanced[4] that the dissolution of gels in high boiling-point solvents is due to disruption of chemical bonds by swelling forces. It is shown that this leads to the concept of a definite temperature at which the swollen gel will be completely disrupted by the swelling pressure of the solvent, and it follows that the temperature will vary with the degree of swelling, decreasing with increased swelling; and will, therefore, depend on the nature of the polymer-solvent interaction. In the work now reported, no examination of dissolution below temperatures of 150° C has been made, and the question of a definite temperature of dissolution remains open. It is, however, quite certain that, at the rates here reported, oxygen is an essential intermediary, but this does not rule out the possibility that the process is essentially as predicted theoretically by Tobolsky[5], or that a second, much slower, process of that type does not go on in the absence of oxygen.

An alternative approach to an explanation of the process is regarded as more in accord with the experimental evidence. This indicates that scission is contingent upon oxidation. This is probably the rate-determining process. Butyl rubber, where the possibility of reaction with oxygen is much reduced by the relative infrequency of double bonds, reacts most slowly. The chain of reactions comprising the oxidative process in these materials is such that after chain scission, rejoining of the severed ends with some other molecule or part of molecule is likely, and also oxygen can play a dual role and act as a cross-linking agent as well as a chain-scission agent. The net effect will depend on circumstances favoring one type of reaction at the expense of the other. In a solvent favoring dissolution, solvation of the severed portion of a molecule reduces the probability of recombination and favors the scission process. Dissolution occurs after scission if the rubber and solvent mix.

With this picture of the process, the swelling of the dissolved polymer is not a necessary cause of scission, but arises from the same cause that scission is followed by dissolution; namely, that the polymer and solvent are miscible—equally well, whether vulcanized or unvulcanized. The "force" of swelling is not the cause of dissolution, and the amount of swelling is not correlated with the rate of dissolution.

SPECIFIC APPLICATIONS TO ANALYTICAL PRACTICE

We are now in a position to formulate the desirable features for any procedure for the dissolution of vulcanized material. The solvent chosen should

be one that is completely miscible with the polymer at the temperature of dissolution and also at much lower temperatures, if not at room temperatures. It is convenient to boil liquids under reflux instead of using baths at fixed temperatures, and since the boiling point is the highest temperature easily obtainable, a liquid with as high a boiling point as possible should be used. Air should be bubbled through the solution as it boils. The importance of adequate aeration is particularly noticeable in the case of GR-S. If air is excluded, and displacement of air from the vessel used by the boiling vapors seems adequate to exclude air, then continued heating does not result in dissolution, and further, subsequent aeration produces dissolution only at a very slow rate. This would appear to be an example of the well-known cross-linking of GR-S on heating in the absence of air, and prepared samples of cyclised material do show a much reduced rate of dissolution. Inefficient aeration at the commencement of the procedure may result in six or more hours being required to produce the dissolution of GR-S in *p*-dichlorobenzene, even when the efficiency of the aeration is increased after the commencement. Given efficient aeration and miscibility of solvent the rate is largely a function of the rubber, and the temperature and alteration of solvent does not much influence the rate at a given temperature. There is a gain, therefore, in using the solvent of highest boiling point and this is the reason for their use, the rate being extremely slow for temperatures below 100° C. Extrapolation of Figure 2 below 100° C indicates a decrease of rates by factors of between 100 and 1,000. The suggested use of α-nitronaphthalene, with a boiling point of 305° C, is valuable, although its cost may lead to its use being confined to the micro-scale.

For iodine value determination, it is essential to use an aromatic compound with one or more electronegative groups in the nucleus. It is fortunate, therefore, that both polar and nonpolar rubbers are soluble in *p*-dichlorobenzene, which is eminently suitable for this purpose, although it is, of course, necessary to add a second solvent after the dissolution has been completed.

The determination of cellulose content of proofed fabrics or rubber-containing cellulose; e.g., whole-tire reclaim, is frequently carried out by the dissolution of the rubber, followed by filtration. The cellulose remains with the total fillers and is determined by acetylation. In view of the rigorous conditions of the dissolution and of its oxidative nature, degradation of the cellulose must occur and considerable error result from losses. 95 per cent of pure cellulose was recovered after treatment corresponding to the dissolution conditions and, until a better procedure is available, it should be remembered that results of cellulose content obtained must be on the low side by amounts of the order of 5 per cent of that present. In the case of a reclaim, where the cellulose is already degraded, the error is probably greater.

ACKNOWLEDGMENT

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REFERENCES

[1] Kemp and Peters, *Ind. Eng. Chem. Anal. Ed.* **15**, 453 (1943).
[2] British Standard Specification B.S. 903, London, 1940; ASTM "Standards on Rubber Products", American Society for Testing Materials, Philadelphia, 1946.
[3] Eley, *Trans. Faraday Soc.* 1939, p. 35.
[4] Gee, in "Advances in Colloid Science", New York, 1946, Vol. 2, p. 145. This is a general account and also gives references to the original papers of the same author.
[5] Tobolsky, *J. Chem. Physics* 11, 290 (1943).
[6] Wyatt, *Analyst* 66, 362 (1941).

A NEW GRAVITOMETER *

E. F. LINHORST

UNITED STATES RUBBER CO., FORT WAYNE PLANT, FORT WAYNE, INDIANA

Several months ago the Fort Wayne Plant of the United States Rubber Company began to use a new Jolly type of balance for determining the specific gravity of cured rubber. As shown in Figure 1, the apparatus employs two

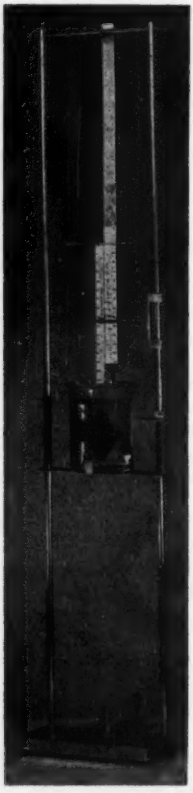


FIG. 1.

springs whose lower ends are joined to a metal rod that supports a moving scale V. A stationary scale A is placed parallel to the scale V. By using two springs instead of one, it is easier to bring the two scales close together.

* Reprinted from the *Review of Scientific Instruments*, Vol. 23, No. 4, page 190, April 1952.

When one places a test sample in a holder at the lower end of scale V, the weight of the sample in air appears on scale A opposite the zero mark of scale V. A movable indicator preserves this reading on scale A. Raising a beaker of water up around the sample raises the V scale until the volume of the sample appears on the V scale under the indicator, which is a thin blade of metal. A slide rule division of the A-scale reading by the V-scale reading gives the specific gravity of the sample. Specific gravities so determined usually agree within 0.5 per cent of those obtained with an analytical balance.

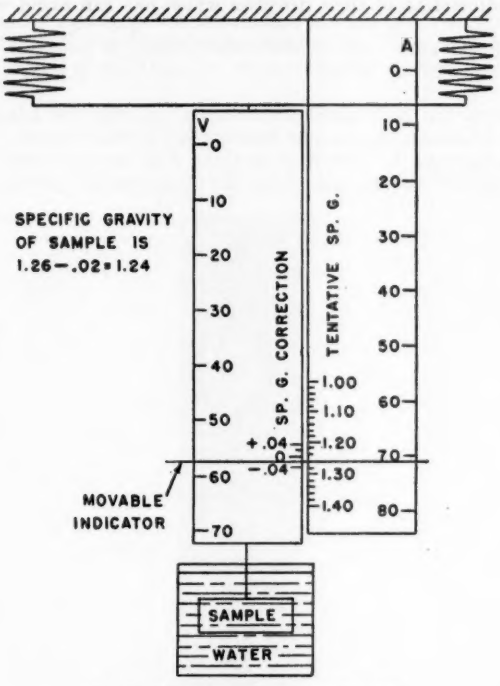


FIG. 2.—Schematic drawing of gravitometer.

The relative accuracy obtained with two springs is essentially equal to that obtained with one spring. Any choice of springs as to elastic rate or load-carrying capacity will depend on the order of magnitude of the weight of the sample.

Test samples in a rubber millroom control laboratory usually have nearly all the same shape and volume, such as a $\frac{1}{4} \times 2 \times 2$ in. rectangular parallelepiped. With this condition the gravitometer can approach being direct reading on a specially constructed scale, shown schematically in Figure 2. The "tentative specific gravity" scale gives the correct reading if the sample has the average volume of such samples on which the scale is based. Immersing the

sample in water usually reveals that the volume does not have the average value and that one must add or subtract a small correction in the second decimal place of the tentative specific gravity. The operator can do this mentally with or without using the indicator.

The new gravitometer has thus reached a point in its development where its speed and accuracy make it ideal for a routine testing laboratory.

The gravitometer has replaced a series of glass jars containing solutions of zinc chloride of graduated densities. The buoyancy of a rubber sample in these solutions yields an estimate of its specific gravity. These solutions require frequent readjustment of their densities which one can avoid with the new apparatus.

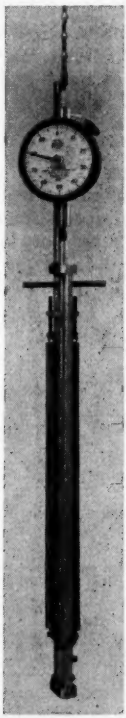
A SIMPLE COMPRESSION PLASTOMETER *

E. F. LINHORST

UNITED STATES RUBBER CO., FORT WAYNE, INDIANA

A new design of a compression plastometer has recently come into use in the Fort Wayne, Ind., plant of United States Rubber Co. The plastometer is used to obtain a measure of the ability of uncured rubber to flow during molding processes.

The apparatus, shown in the accompanying illustration, has two springs that exert a nearly constant force of eight pounds on a sample of uncured rubber held between two round platens, each ½-inch in diameter. A dial gage indicates in mils the thickness of the rubber sample remaining between the platens at any



A Simple Compression Plastometer

* Reprinted from the *India Rubber World*, Vol. 128, No. 5, page 626, August 1953.

time after the test has been started. The sample is originally a disk $\frac{9}{16}$-inch in diameter and about 0.090-inch thick.

In running the test, the operator places the rubber sample between two 400-mesh waterproof emery paper disks $\frac{1}{2}$-inch in diameter, to prevent slippage, and inserts the resulting sandwich between the platens. The dial of the gage is adjusted so that it shows a zero reading when the two disks of emery paper are placed between the platens, and thereafter the gage indicates the thickness of the rubber sample alone. A $\frac{1}{4}$-inch round crossbar that passes through a $\frac{1}{4}$-inch spring-actuated plunger rod enables the operator to separate the platens with index and middle finger while pressing with his thumb on the top of the frame of the plastometer. As soon as the sample has been inserted and the pressure applied, the operator immerses the lower end of the plastometer to a depth of about five inches in a bath of glycerol or some other suitable liquid held at a proper temperature, which may be 250° F, and thermostatically controlled. The sample quickly softens and flows out between the platens, decreasing in thickness until initial curing or scorching stops the flow. In rapidly curing stocks the thickness usually approaches a constant value of about 10 to 30 mils in less than 15 minutes at 250° F.

The measurement to be used for comparison purposes may be the thickness reached in a given time or the time required to reach a certain thickness. A particular stock used in a particular mold may have a critical five-minute plastometer reading below which it molds well and above which it does not. The test with this plastometer provides, therefore, a relatively simple, rapid, and accurate test for predetermining the moldability of a batch of uncured rubber stock.

By a change in the temperature at which the test is run, or in the pressure between the platens, the apparatus can be adapted for the testing of relatively soft or hard materials. Thus an informative test can be made on a sample of uncured sponge rubber at room temperature in five minutes. The plastometer has also been used to give useful data on the hardness of such plastics as the cellulose esters.

NOTE ON THE ADJUSTMENT OF MOONEY VISCOMETER DIE CLOSURE *

GEORGE E. DECKER

RUBBER SECTION, NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C.

During the past ten years, considerable progress has been made in standardizing the Mooney viscometer and in improving the reproducibility of measurements from one instrument to another. The method for adjusting the viscometer die closure developed by Taylor[1] was a major contribution in this respect. In this procedure the die closure adjustment is obtained by setting a specified distance between the mating surfaces of the die holders with feeler gauges and then turning the top guide rod nuts down $\frac{1}{12}$ turn to obtain the desired pressure between the die holders. The chief disadvantages of this procedure are: (1) the $\frac{1}{12}$ turn of the guide rod nuts must be estimated by the operator; (2) the guide rods move sideways in the holes in the bridge when the nuts are loosened, and (3) the threads on the guide rods are not uniform. A modified procedure providing a more accurate and reproducible adjustment is described.

This procedure uses a special cylindrical gauge block (*a* in Figure 1) to replace the lower die during the operation of setting the distance between the mating surfaces of the die holders. Since the gauge block is 0.008 inch thinner than the lower die at the shoulder, adjustment of the die closure by this method will produce a total deformation of 0.004 to 0.006 inch in the various members

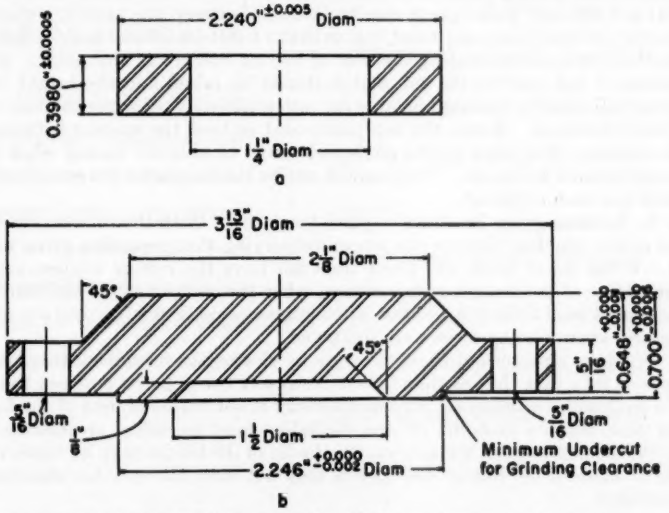


FIG. 1.—Gauge blocks for use in adjusting Mooney viscometer die closure.

(*a*) For use with two-piece die and die holder. (*b*) For use with integral die and die holder.

* Reprinted from the *ASTM Bulletin*, No. 195, pages 51–52 (TP13-14), January 1954. This work was performed as part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government synthetic-rubber program.

of the linkage, as recommended by Taylor[1]. When this method of die closure is used in connection with the integral die and die holders, which are described elsewhere[2], the integral gauge block illustrated at *b* in Figure 1 is used.

Use of this procedure at the National Bureau of Standards and in the Government synthetic rubber plants during the past two and one-half years has resulted in considerable improvement in the accuracy and reproducibility in die-closure adjustments.

ADJUSTMENT OF DIE CLOSURE

The improved procedure is as follows:

1. Make sure that the dies and die holders are clean and properly installed and the temperature of the viscometer is at 212° F. Adjust the bridge so that it is parallel with the top platen and align the linkage so that all the pins are on a common centerline when the viscometer is closed.

2. Remove the lower die and replace it with one of the gauge blocks shown in Figure 1. Care should be exercised in tightening the cap screws in order that the die holder is not deformed by having one screw tighter than another or by having all the screws too tight.

3. Place four coil springs between the platens, one at each corner. These springs should have a free length of 2½ inches, a minimum deflection of 1¼ inches, a spring constant of about 130 lb. per in., and have flat and ground ends. Suitable springs having a ¾-inch pitch can be made by winding ⅛-inch spring wire on a 0.66-inch diameter mandrel.

4. Lower the top platen with the springs in place and measure the distance between the mating surfaces of the die holders. This distance should be such that a 0.002-inch feeler gauge can be inserted between the mating surfaces of the die holders *at some one point*, but so that a 0.004-inch feeler gauge cannot be inserted between the mating surfaces of the die holders at any point. If this spacing is not correct, the top platen should be raised and the height of the bridge adjusted by turning the nuts on both guide rods the same amount in the desired direction. Lower the top platen and recheck the spacing between the die holders. The nuts on the guide rods must be securely locked when these measurements are made. They should not be loosened after the proper adjustment has been obtained.

5. Remove gauge block and replace lower die. With the rotor in place and the motor running, tighten cap screws (observing the precaution given in step 2). If the lower die is one which does not have the rubber washer, and the fluctuation of the dial gauge is increased when the cap screws are tightened, the die should be shifted to a position at which the periodic fluctuations are not increased when the cap screws are tightened.

6. Make a pattern of the die closure by closing the machine after placing a piece of thin (not thicker than 0.0015 inch) soft tissue paper between the dies. If a continuous pattern of uniform intensity is not obtained, one of the following items may be at fault: (1) the die holder may be cocked or deformed due to uneven tightness of the screws, (2) the lip of die holder may be worn, or (3) one or more of the dies or die holders may not meet the specified dimensional tolerances.

7. If it is necessary to change the position of either die holder or to replace any of the parts in order to obtain a desired die pattern, the die closure should be readjusted.

REFERENCES

[1] Taylor, *India Rubber World* 112, 582 (1945); National Bureau of Standards, Circular C451 (1945); Rubber Chemistry & Technology 19, 808 (1946).
[2] Decker and Roth, *India Rubber World* 128, 339 (1953).

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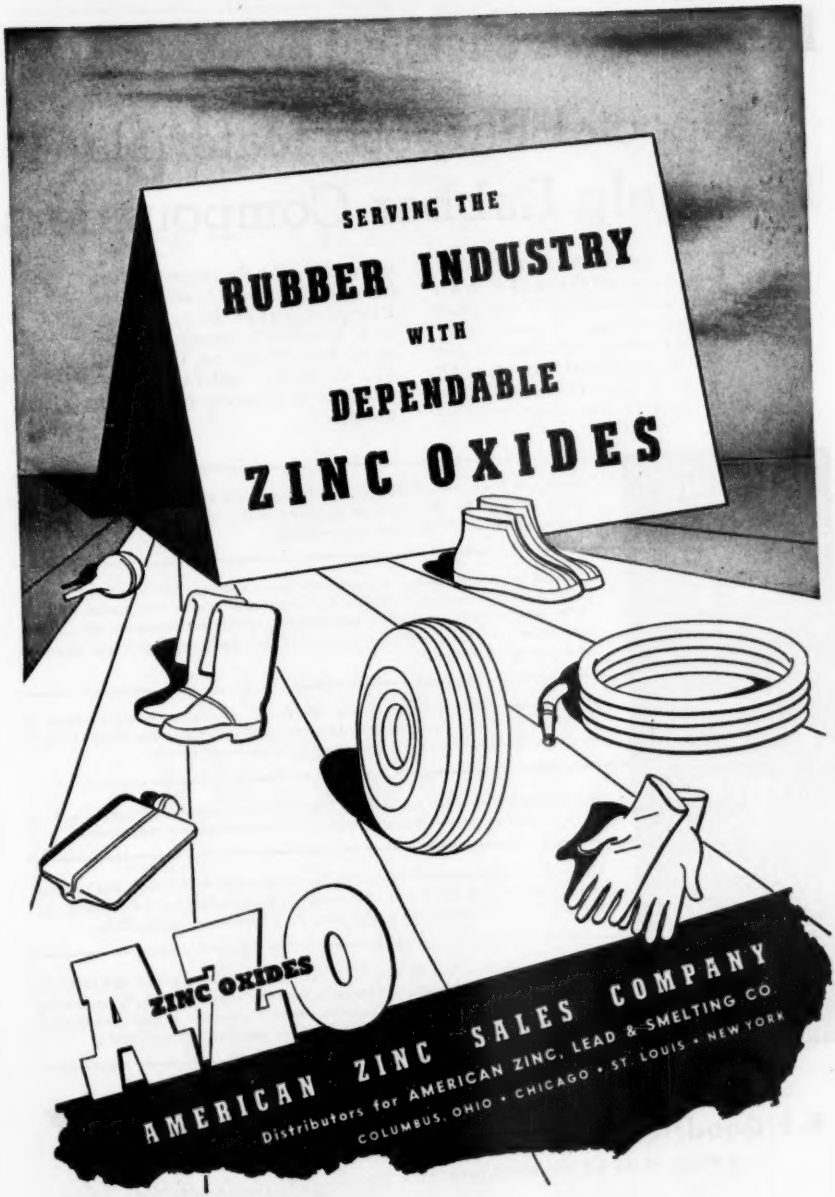
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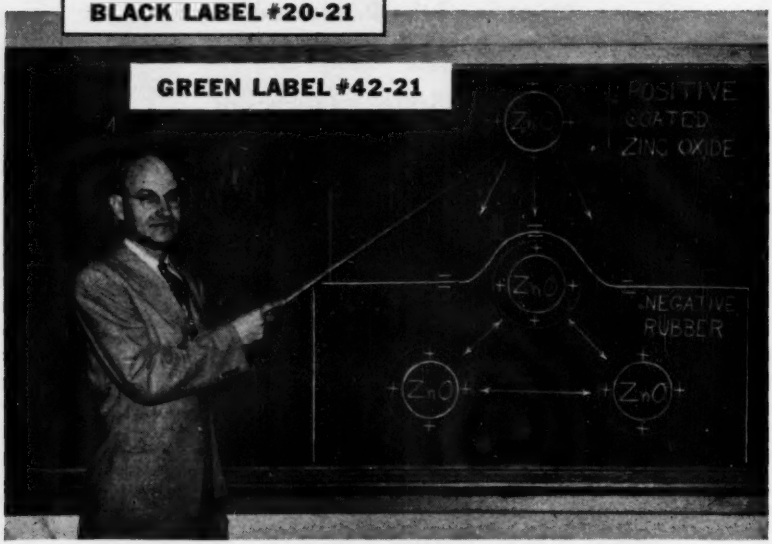

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